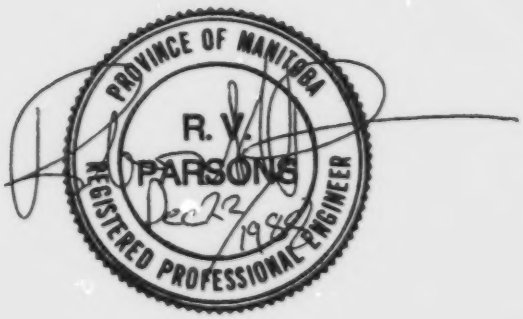
Bioenergy Development Program
Renewable Energy Branch
Energy, Mines and Resources Canada

Development of an Energy Efficient, Membrane Recovery System Suitable for Ethanol from Cellulose Processes



December, 1988

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DEVELOPMENT OF AN ENERGY EFFICIENT MEMBRANE RECOVERY SYSTEM SUITABLE FOR ETHANOL FROM CELLULOSE

RENEWABLE ENERGY BRANCH

PREPARED FOR:

Bioenergy Development Program
Renewable Energy Branch
Energy, Mines and Resources Canada
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PREFACE

In the production of ethanol from biomass via fermentation, the purification of the ethanol product is an important consideration. The final ethanol content of a fermentation broth or beer is dilute, with a concentration of no more than about ten weight percent. The ethanol thus must be purified to an anhydrous product before it can be employed in motor fuel as an octaine enhancer or fuel extender.

The standard separation technology employed today is distillation. Distillation is essentially a temperature driven process, which exploits the greater volatility of ethanol relative to water. This effect can be expressed in terms of vapour-liquid equilibrium.

While the distillation process is well established, it can be expensive. Upwards of 20 percent or more of total energy requirement and 20 percent of the capital cost of producing ethanol in present conventional ethanol production facilities are for distillation, and distillation costs are very sensitive to the concentration of ethanol in the feed beer. As the ethanol content in the beer decreases, the energy and capital cost requirements for distillation escalate rapidly.

This situation is exacerabated when cellulosics are employed to produce ethanol, since such substrates have tended to be very dilute. In cellulose hydrolysis, high sugar concentrations can only be achieved at the expense of conversion efficiency.

Separation of ethanol and water by distillation is also limited by the presence of a low boiling point binary azeotrope at 95.6 weight percent ethanol. Because the composition of vapour and liquid at the azeotrope are identical, ethanol cannot be purified beyond this point by simple staged atmospheric distillation. The conventional method employed for this final dehydration step is so-called "azeotropic distillation". This process involves the addition of a third component or entrainer such as benzene, pentane or cyclo hexane to disrupt the binary equilibrium. Azeotropic distillation is, however, very energy intensive, requiring almost one third of the total energy needed to purify ethanol.

Membrane processes, unlike distillation, exploit selective adsorption and selective transport of molecules. They employ pressure as the driving force, rather than temperature in the case of distillation. Thus membranes have been viewed in general as a means of achieving more energy efficient separation of ethanol and water.

The initial objective was to investigate and develop a membrane process to selectively transport and concentrate ethanol from water in the vapour phase. It was anticipated that if the selective recovery of ethanol proved successful, it would, by reducing total separation energy requirements, allow more dilute substrate streams to be employed in fermentation, and thus allow emphasis in the hydrolysis of cellulosics to shift more toward increasing the conversion efficiency.

The initial objective of the study was not achieved because sufficient selectivity to ethanol could not be attained. However, during the course of screening experiments, very encouraging water selectivity and solvent resistance were found for a newly developed hydrophilic polymer, carboxylated udel polysulfone. This material showed good potential to be employed for water selective dehydration of ethanol/water mixtures in the vapour phase. It was thus recommended that additional development work be conducted using this polymer material.

ABSTRACT

The initial objective of the study was to work toward the development of an energy-efficient membrane based ethanol recovery process, involving selective permeation and concentration of ethanol. A variety of membranes, polymer films and films incorporating selective agents were tested for selectivity to ethanol in membrane test systems using ethanol/water vapour feed mixtures.

The initial objective was not achieved because sufficient selectivity to ethanol could not be attained. However, very encouraging water selectivity and solvent resistance were found for a novel hydrophilic polymer, carboxylated udel polysulfone, developed by the National Research Council of Canada. This material showed potential to be employed for dehydration of ethanol/water mixtures in the vapour phase, and it was recommended that additional development work be conducted using this polymer material.

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EXECUTIVE SUMMARY

Membrane processes are viewed in general as a potentially energy-efficient means of separating and purifying ethanol from a dilute fermentation broth. The standard separation technology employed in the ethanol industry is distillation. The energy requirements and capital cost of distillation increase dramatically as the concentration of ethanol in the feed beer becomes more dilute. This is especially problematic when cellulosic substrates are employed, since higher sugar substrate concentrations can only be achieved at the expense of conversion efficiency. Distillation is also limited by the presence of a binary ethanol/water azeotrope, which necessitates the use of costly, and energy intensive azeotropic distillation in order to obtain an anhydrous product.

The objective of the study was to develop a potential commercial process for energy-efficient concentration of ethanol using membranes selectively permeable to ethanol in the vapour phase. Unfortunately, this objective could not be achieved because sufficient selectivity to ethanol could not be attained. Very encouraging results were obtained, however, for vapour phase dehydration of ethanol/water mistures using water selective membranes made of a newly developed, modified polysulfone polymer from the National Research Council of Canada (NRCC).

Work was conducted for this project at the Laboratories of the Chemical Engineering Section of NRC. Initially, this project was to involve screening of available membranes and materials to confirm vapour phase ethanol selectivity followed by development of high performance membranes, possessing both high flux and high selectivity. Acceptable ethanol selectivity could not, however, be achieved, which was disappointing, and the project did not proceed past the screening stage. A number of different approaches were employed without success. These included the addition of ethanol selective extractant agents, which were selected with the assistance of Queen's University, and the addition of selective zeolites.

While the results of this work cannot preclude that an ethanol selective vapour phase membrane process is possible, two major problems became apparent through the course of the study:

1. The first and most important was the lack of selectivity toward ethanol in even very hydrophobic polymer materials. There also appeared to be a strong inherent dependency of selectivity on temperature and concentration, both of which appeared to work against the selective concentration of ethanol.

2. The second but also major problem was one of materials incompatability of polymers to the high temperature vapour ethanol environment.

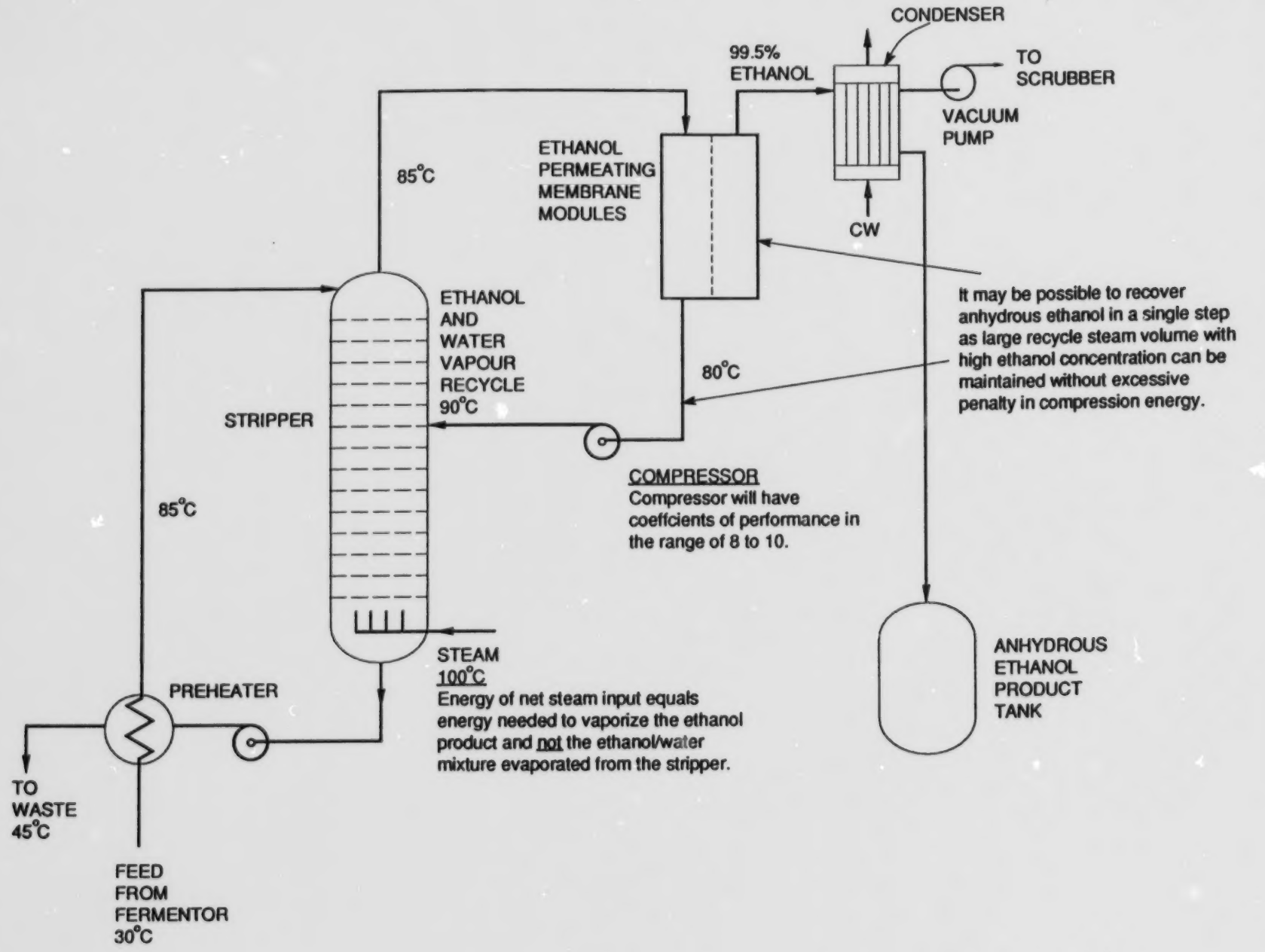
While the major purpose of the project could not be achieved, some very successful results were obtained with potential for commercial development using water selective membranes.

The Chemical Engineering Section of NRC has recently developed a new generation of modified Udel polysulfone membrane polymers with specific added

functionalities. While Udel polysulfone itself would not stand up to vapour ethanol at the temperatures involved, and was found to fail in a catastrophic manner, one of these modified polysulfones, specifically the carboxylated Udel polysulfone, exhibited good resistance to the solvent ethanol environment. Although runs conducted with this hydrophilic material were still preliminary, they also confirmed that it exerted a strong selectivity toward water. Experimental results also indicated that selectivity toward water might be related to the degree of carboxyl group substitution, suggesting that the selectivity to water could be improved.

Carboxylated polysulfone is a completely novel polymer that may compete favourably with other developing technologies in vapour phase dehydration of ethanol. Additional testing and development work employing this polymer material were recommended on the basis of the results obtained in this study.

RESUME



PROCESS FOR ETHANOL RECOVERY

FIGURE 1

1.0 INTRODUCTION

This study was conducted under the auspices of the Bioenergy Development Program, for the development of a novel, energy efficient membrane-based separation process that would be applicable to the production of ethanol via fermentation from cellulosic substrates.

The initial intent was to seek membranes that would be selective to ethanol in the vapour phase, and a variety of membranes, polymer films, and selective additives were screened in test assemblies. The project did not proceed past this initial stage, first because sufficient vapour phase selectivity to ethanol could not be achieved, and secondly because of materials incompatibility with the high temperature ethanol vapour environment.

Favourable observations were made with water selective, modified polysulfone films, potentially suitable for vapour phase dehydration, and in the closing portions of the project more emphasis was placed on testing these materials.

2.0 OBJECTIVES

The initial objective of the study was to develop an energy-efficient membrane based ethanol recovery process. The proposed process concept, as illustrated in Figure 1, involved two novel tactics:

1. Development and use of membranes selective to an organic (i.e. ethanol) from water, such that there would be an enhancement in the concentration of ethanol product in the membrane permeate.

2. Operation of membranes with the feed stream in the vapour phase.

It was intended that this process would have application to ethanol-from-cellulose conversion technologies. In cellulose hydrolysis, using either acids or enzymes, high final glucose concentrations can only be achieved at the expense of conversion efficiency. It was anticipated that if the ethanol recovery process proved successful, it would reduce total distillation energy requirements, thus allowing the use of more dilute sugar streams and as a consequence allowing emphasis in hydrolysis to shift away from maximizing sugar concentrations toward increasing the efficiency of cellulose conversion.

The activities that were to be performed in this phase of the project are described as follows:

1. Testing of available ethanol permeable membranes and materials under vapour phase to establish the validity of the process concept.

2. First phase of development of ethanol specific membranes with acceptable permeability and selectivity.

3. Feasibility analysis to demonstrate the application of the

technology and its benefits for ethanol from cellulose.

The process approach employed in the project was very novel, using in essence a kinetic type phenomenon in the form of interactions with a membrane to overcome thermodynamic limitations. It was conjectured that it might be possible to recover virtually anhydrous ethanol in a single step. And while the selectivity behaviour of membranes for vapours at elevated temperatures was largely unknown, there was optimism that the desired selectivity could be achieved.

The information available from the literature on ethanol/water vapour separations was very limited. The few papers published, as well as known commercial development activity being conducted by Monsanto, however, were directed toward water selective membrane systems suitable for vapour phase dehydration. The closest parallels for organoselective type behaviour seemed to be in pervaporation, which is described in the following section. While selectivity for ethanol from water in pervaporation was rare as evidenced by its infrequent mention in the literature, it was noted to be possible to a limited extent by using rubbery type polymers, especially silicone (polydimethylsiloxane). Operation with the feed in vapour phase appeared to be the obvious extension of such work for the elimination of liquid film resistances and potential improvement in selectivity to ethanol. A confirmation of such thinking with respect to pervaporation appeared in the literature just at the initiation of the project in Rautenbach and Albrecht (1987), as follows:

> "An interesting modification of the process, which must be investigated in more detail, consists of using a feed stream of vapor, e.g. the vapor from a rectification column. The problem of phase change is then avoided. Since the principle of separation in pervaporation, namely, a lowering of the activity on the permeate side of the membrane by the application of vacuum, is retained, the driving potential for separation is retained to a large extent. Because of the large diffusion coefficients in vaporous mixtures, the mass transfer resistances at the feed side of the membrane are small compared to conventional pervaporation."

3.0 BACKGROUND

3.1 Membranes

The study involved the use of various polymer films and membranes in an attempt to perform selective separations. While semipermeable homogeneous films have been known and examined for a fairly long time, virtually all present commercially feasible membrane processes have been made possible by the advent of thin-skinned asymmetric membranes, since in virtually all membrane applications flux is inversely proportional to membrane thickness.

The development of such membranes, which involve a very open porous substructure with a thin dense surface layer responsible for selectivity, dates back to the still relatively recent innovation of high flux reverse osmosis membranes by Loeb and Sourirajan in the 1950's. The evolution and characteristics of thin-skin asymmetric polymer membranes, as well as various present manufacturing techniques, are described briefly in Lonsdale (1987).

As discussed in the next section, the vapour phase separation process most parallels conventional gas separation. In gas separation, which requires a selective, defect-free membrame surface, there are generally three variations of asymmetric membranes employed, as described for instance in Baker and Blume (1986) or Matson et. al. (1983), as follows:

1. Integrally skinned asymmetric membranes, where the skin layer of polymer provides for selectivity and sealing.

2. Thin-film composites or TFC's, where an ultra thin surface layer of selective polymer is added on the surface.

3. Coated asymmetric membranes, where the membrane substrate provides the selectivity, with a thin, fairly unselective surface coating layer to seal defects.

Another quite different approach employed in the case of gas separation is the so-called "Liquid Membrane", as also described in Matson et. al. (1983), in which a selective liquid is immobilized in the membrane pores or resides on the membrane surface.

While a number of asymmetric membranes were employed, testing was conducted predominately with dense homogeneous films. Some "Liquid Membrane" type films were also made and tested.

3.2 Membrane Processes

Membrane processes are classified by the nature of the phase of the feed and permeate, and in aqueous systems according to approximate size of membrane "pores". For the separation of small ethanol and water molecules in vapour phase there are three other relevant membrane processes to be considered, which are described briefly as follows:

1. Reverse Osmosis

Reverse osmosis or hyperfiltration is a common membrane separation process in which the feed and permeate are both in the liquid phase. The effective pore size is so small that only the solvent, i.e. water, is desired to pass through. Aqueous phase interactions between the solute, in this case ethanol, and the solvent necessitate the use of high pressures in order to overcome osmotic pressure, and hence the name reverse osmosis. In the case of ethanol and water, the osmotic pressure is very high and thus very high feed pressures are required to achieve any appreciable rejection (term described below) of the solute. While reverse osmosis is a totally aqueous process, the concepts and models for pore transport of small molecules have generally been derived from reverse osmosis.

2. Pervaporation

In pervaporation or transmembrane permeation evaporation, the feed on the upstream side of the membrane is liquid while the permeate is vapour, usually created by vacuum.

3. Gas Separation

The closest parallel to separation of vapours is more conventional gas separation, where both feed and permeate are in the gaseous or vapour state. Gas separation is described in more detail in Matson et. al. (1983). There are however significant differences. In vapour separation the interactions between the species, as represented by vapour-liquid equilibrium, are much more important.

3.3 Mechanisms and Models

In the separation of small molecules by reverse osmosis, pervaporation or gas separation, there have been a number of approaches proposed to describe the transport mechanisms which, as summarized for instance by Mazid (1984) for reverse osmosis, all basically involve pore flow and/or diffusive flow. The two most prominent mechanisms are the simpler Solution-Diffusion model, and the more descriptive Preferential Sorption-Capillary Flow mechanism.

Solution-Diffusion essentially assumes the membrane material to be a continuum onto which the species adsorb in a manner described by Henry's Law, and then diffuse through according to a simple Fickian rule. This model can be developed simply as follows:

$$J_i = D \frac{dC_i}{dX} \text{ (Fick's Law)}; \quad x_i = p_i/K \text{ or } p_i S \text{ (Henry's Law)}$$

so that

$$J_i = D\ S\ (p_{i_2} - p_{i_1})/l$$

where:

J_i	=	Flux
D	=	Diffusivity
C_i	=	Concentration
p_i	=	Partial Pressure
l	=	Thickness
1/S or K	=	Henry's Law constant

This model is useful in defining the so called Permeability or "Permeability Coefficient" parameter, P, as follows, which is widely quoted in the literature to describe pure component gas permeation through polymers:

$$P = D\ S = \frac{J\ l}{\Delta\ p}$$

This quantity is usually expressed in units of cm^3 cm/cm^2 s cmHg and is very easy to determine for simple gases. The temperature dependence of the permeability coefficient is frequently discussed in the literature and is usually described by an Arhennius type relationship, as follows:

$$P = P_o\ e^{-(E/RT)}$$

where: E is an activation energy for a given permeant and polymer

Permeability coefficient values have also been quoted for vapour permeation through polymers, however, in this case, as opposed to simple gases, the method of determination is much less easy, as presented in Rogers et. al. (1972), and the utility of the term is more doubtful. The more obvious and important interactions between vapour solutes and polymer, as evidenced by swelling, as well as between different solute components, point out weaknesses of the assumption of ideal, Henry's Law adsorption. As mentioned in Rogers (1985), other relationships to describe adsorption including the Langmuire, Flory-Huggin, and BET equations can be employed, and various of these have been used in the literature (although not discussed further here.)

The Preferential Sorption-Capillary Flow approach, unlike Solution-Dilution, visualizes pores on the membrane surface. The model introduces concepts of more complex interactions, as well as pore size distribution. In vapour phase separation of ethanol and water there are a variety of potential mechanisms that could come simultaneously into play when pores are considered. These can be classed as in Asaeda and Du (1986) into four categories as follows:

1. Knudsen diffusion
2. Surface adsorption and diffusion
3. Capillary condensation with liquid flow

4. Molecular sieving

It is important to note that if the larger ethanol molecule were to be separated selectively from the smaller water molecule only those mechanisms involving selective adsorption (i.e. No.'s 2 and 3) could be relied upon.

Both the Solution-Diffusion and Preferential Sorption-Capillary Flow models share the characteristic of describing the transport process in two parts: first adsorption and secondly transport, with adsorption usually considered to be the dominant effect. Another common characteristic unfortunately shared by these models is the assumption of non-interaction of the species to be separated. Separations are presumed to occur because of differences in the independent interactions of each species with the membrane polymer. In the case of ethanol-water mixtures, there is a strong association between the two species.

Other questions relating to ethanol/water vapour separations remain unresolved in currently understood mechanisms and presumed models. It is not known whether condensation occurs in pores (and if so in what temperature range), nor whether the species preferentially adsorbed by the membrane polymer is actually the one passed through the membrane preferentially.

3.4 Separation Nomenclature

The nomenclature used to express separations of vapour species by membranes is sometimes confusing. Slightly differing terms are usually employed for each of related membrane operations of reverse osmosis, pervaporation and conventional gas separation, and, due to overlap, all could have some application.

For a system under consideration, the concentrations of species to be separated can be expressed as follows:

x = fraction (mass) of component in feed
y = fraction (mass) of component downstream of membrane
i,j = respective components

In Reverse Osmosis, separation is expressed as "Rejection", which is defined as follows, usually as a percentage:

$$\text{Rejection} = (x_i - y_i)/x_i$$

In this case, compositions are often expressed as weight per unit volume measures.

In Pervaporation, the term usually employed is the "α" separation factor, also called "Separation Factor" or "Selectivity", which is defined as follows:

$$\alpha_{ij} = \frac{(y_i/y_j)}{(x_i/x_j)} \qquad \text{(Membrane Separation Factor)}$$

This term is dimensionless and is independent of whether units are expressed on a mass or mole basis. Sometimes the "x" terms are represented by the concentrations of species in the retained non-permeate, but more usually are represented as feed concentrations. As permeate flux becomes smaller relative to the feed rate, these cases approach one another, and become essentially equivalent.

The attraction of the α_{ij} expression is its homology with Relative Volatility, which can be used to characterize equilibrium separations such as distillation. This latter term is defined in the same way but with y and x representing vapour and liquid fractions respectively, as follows:

$$\alpha_{ij} = \frac{(y_i/y_j)}{(x_i/x_j)} \qquad \text{(Relative Volatility)}$$

In an ideal mixture where Raoult's and Dalton's Laws laws are obeyed, and thus $p_i = p_{yi} = p_{oi}\, x_i$, where p_{oi} is the saturation vapour pressure of component i, this term reduces to the following relationship, from where it derives its definition as Relative Volatility:

$$\alpha_{ij} = p_{oi}/p_{oj}$$

$$\text{or} = (\gamma_i\, p_{oi}/\gamma_j p_{oj})$$

where there is deviation from Raoult's Law and
where: γ = Liquid Phase Activity Coefficient

A less frequently employed term used to describe separation in Pervaporation is the so-called "β" separation factor, which is defined as follows:

$$\beta = y_i/x_i$$

This term can also be related to one used to describe equilibrium processes, in this case the Equilibrium or Distribution Ratio.

In conventional gas systems, separations are most often represented by component gas permeability ratios as follows:

$$\alpha_{ij}^{*} = P_i/P_j$$

Very often such numbers are presented in the literature as ratios of independently determined pure component permeabilities. In this case, such ratios are useful only as a guideline of what can be expected.

An expression to relate this ratio to the α_{ij} separation factor defined above can be derived for instance by starting with a ratio of

component fluxes and assuming a solution-diffusion mechanism as presented in Kirk-Othmer (Volume 15, p118). This relationship is presented as follows, p_1 and p_2 are the total pressures on the feed and downstream sides of the membrane respectively:

$$\alpha_{ij} = \alpha_{ij}^{*} \frac{(1 - (p_2 y_i / p_1 x_i))}{(1 - (p_2 y_j / p_1 x_j))}$$

From this relationship, it can be seen that when feed pressure is much greater than downstream pressure ($p_1 >> p_2$), then α_{ij} tends to α_{ij}^{*}. However, at finite pressure differences $\alpha_{ij} < \alpha_{ij}^{*}$, making the permeability ratio in essence an upper limit of possible separation. This relationship also does not take into account interaction between species, which would be usually expected to further reduce the actual separation.

Thus it can be seen that for membrane operations similar to vapour separation, different methods are employed to report separation. It was decided that for the purposes of this study the α_{ij} separation factor would be used.

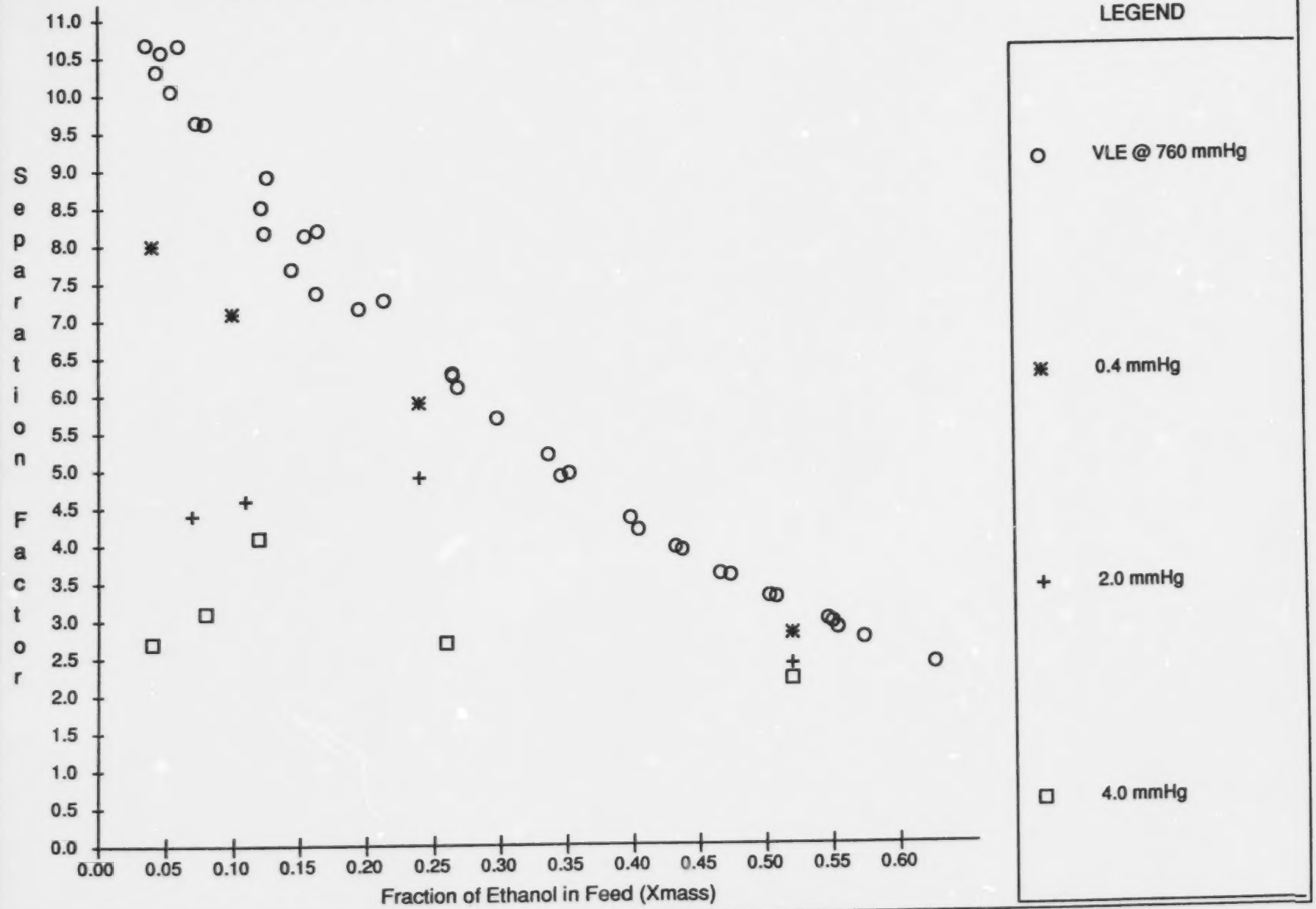
As discussed previously, the temperature dependence of permeability coefficients is usually described by an Arhenius type relationship, and it is thus appropriate to describe the temperature dependence of the separation factor in a similar manner, as follows:

$$\alpha_{ij} = k_1 \, e^{-(k_2/RT)}$$

where: k_1 and k_2 are Constants

Figure 2. Estimated Pervaporation Data of Baker and Blume (1987) for Silicone Rubber

Separation Factor [αew] Values as a Function of Total Permeate Pressure



4.0 ETHANOL/WATER SEPARATION LITERATURE

Membrane systems, in general, have been viewed as a means to potentially improve the energy efficiency of producing ethanol. Conventionally, ethanol is recovered by the distillation of fermentation broths, where it is present in concentrations from about three to ten percent. This process which relies on staged vapour-liquid equilibrium is energy intensive and limited by the presence of a low boiling point binary azeotrope at 95.6 weight percent ethanol.

Typically, ethanol is concentrated to the range of 92-94 percent by stripping and subsequent rectification, followed by azeotropic distillation employing an entrainer such as benzene or pentane to disrupt the binary equilibrium and allow concentration of the ethanol to an anhydrous product of 99 plus percent. A comparative summary of energy consumption by a variety of separation processes is presented in Campbell (1983, p80), with the energy requirement for concentration from 10 to 95 percent ethanol by distillation approximately 5 GJ/m^3 (anhydrous product), while energy requirements of azeotropic distillation to go from 95 to 100 percent ethanol approximately 2.6 GJ/m^3 (anhydrous product).

Leeper (1986) has provided a fairly comprehensive review of all types of membrane processes applied to ethanol recovery, including discussion on reverse osmosis, pervaporation, and vapour separation.

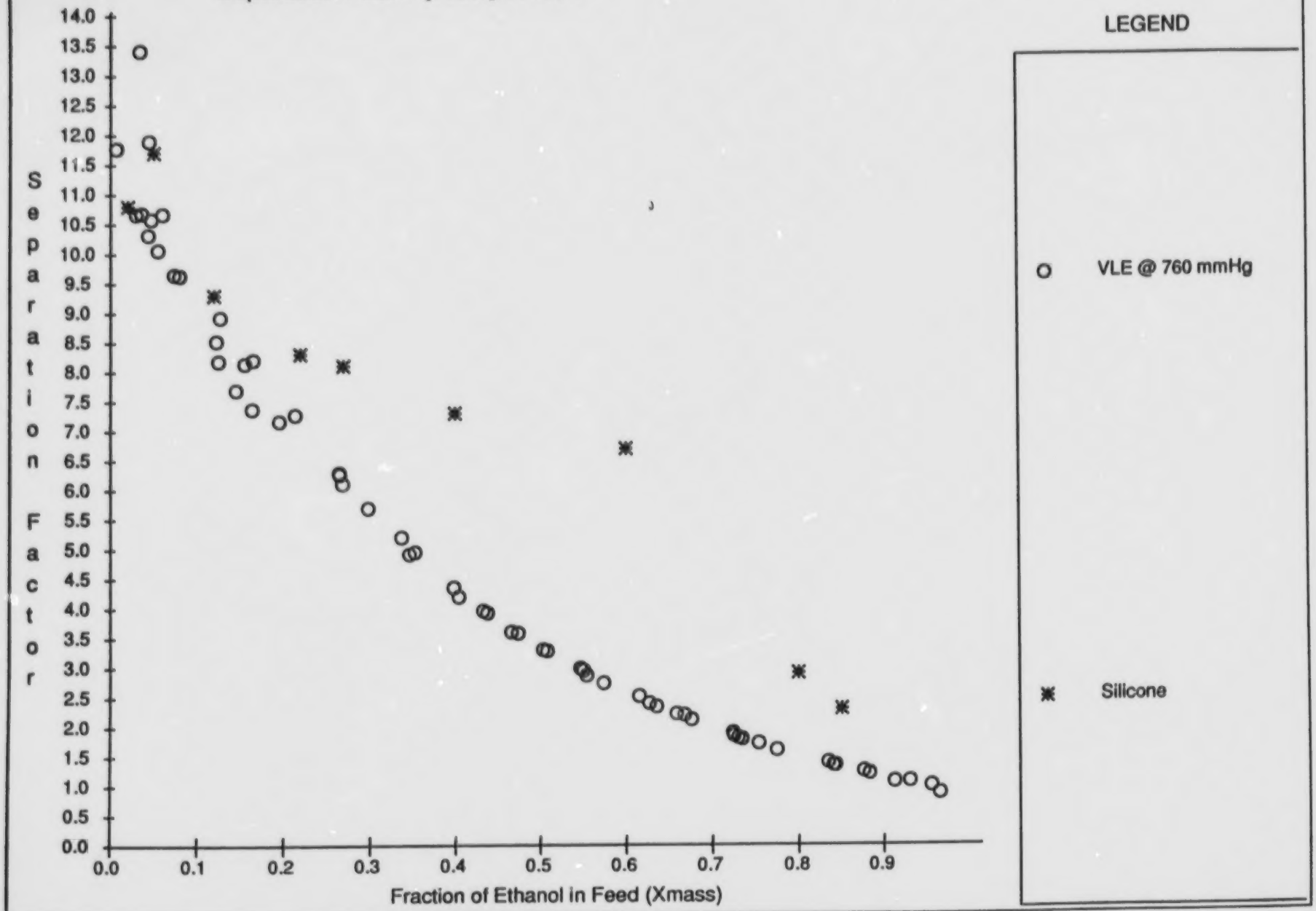
While not specifically relevant to this study, much attention has been focused on reverse osmosis. Given the very high osmotic pressures involved in ethanol/water mixtures, most potential for the application of available RO membranes is considered, as suggested for instance in Mehta (1982) or Leeper and Tsao (1987), to be in preconcentration of low alcohol content beers prior to distillation.

The large majority of work in pervaporation has been directed toward water selective membranes, with intended application to dehydration of azeotropic ethanol/water mixtures. In this regard, one such system has already been commercialized employing GFT's composite polyvinylalcohol on porous polyacrylonitrile membranes and being marketed through Vogelbush. As indicated in Sodeck and Hannak (1986), several such plants of 1,000 and 2,000 L/day capacity have been operated since 1984.

Apparent ethanol selective behaviour in pervaporation, although much less frequent, has been reported. While other materials have exhibited such behaviour, the clear standout in the number of citations was silicone rubber or polydimethylsiloxane. Ethanol selective pervaporation using silicone has been reported in the following:

Eustache and Histi (1981)
Kimura and Nomura (1982)
Hoover and Hwang (1982)
Goncalves et. al. (1983)
Mulder et. al. (1983)
Changluo et. al. (1987)

Figure 3. Estimated Pervaporation Data of Kimura and Nomura (1982) for Silicone Rubber



Nakao et. al. (1987)
Blume and Baker (1987)
Suematsu et. al. (1987)

Silicone exhibits dramatic organoselective behaviour in pervaporation to some species such as benzene and 1,2 dichloroethane, as noted in Eustache and Histi (1981). Its apparent selective behaviour toward ethanol, however, may be deceptive. As suggested in Blume and Baker (1987), silicone may really be marginally water selective in pervaporation with any apparent selectivity to ethanol an artifact of vapour-liquid equilibrium. As evidence of this suggestion, they showed, as illustrated in Figure 2, that selectivity to ethanol was always below what could be achieved by equilibrium alone at low pressures, and further that it decreased as the permeate side pressure was dropped closer to absolute vacuum. In all but one notable exception, ethanol selectivities reported in the other articles were found to be no better than what could be achieved by simple equilibrium. The exception was Kimura and Nomura (1982) in which substantially higher selectivities were reported over part of the feed concentration range as illustrated in Figure 3. One common observation, however, was that selectivity to ethanol decreased at high ethanol concentrations to the extent that virtually no ethanol selective membrane behaviour was apparent near the azeotrope.

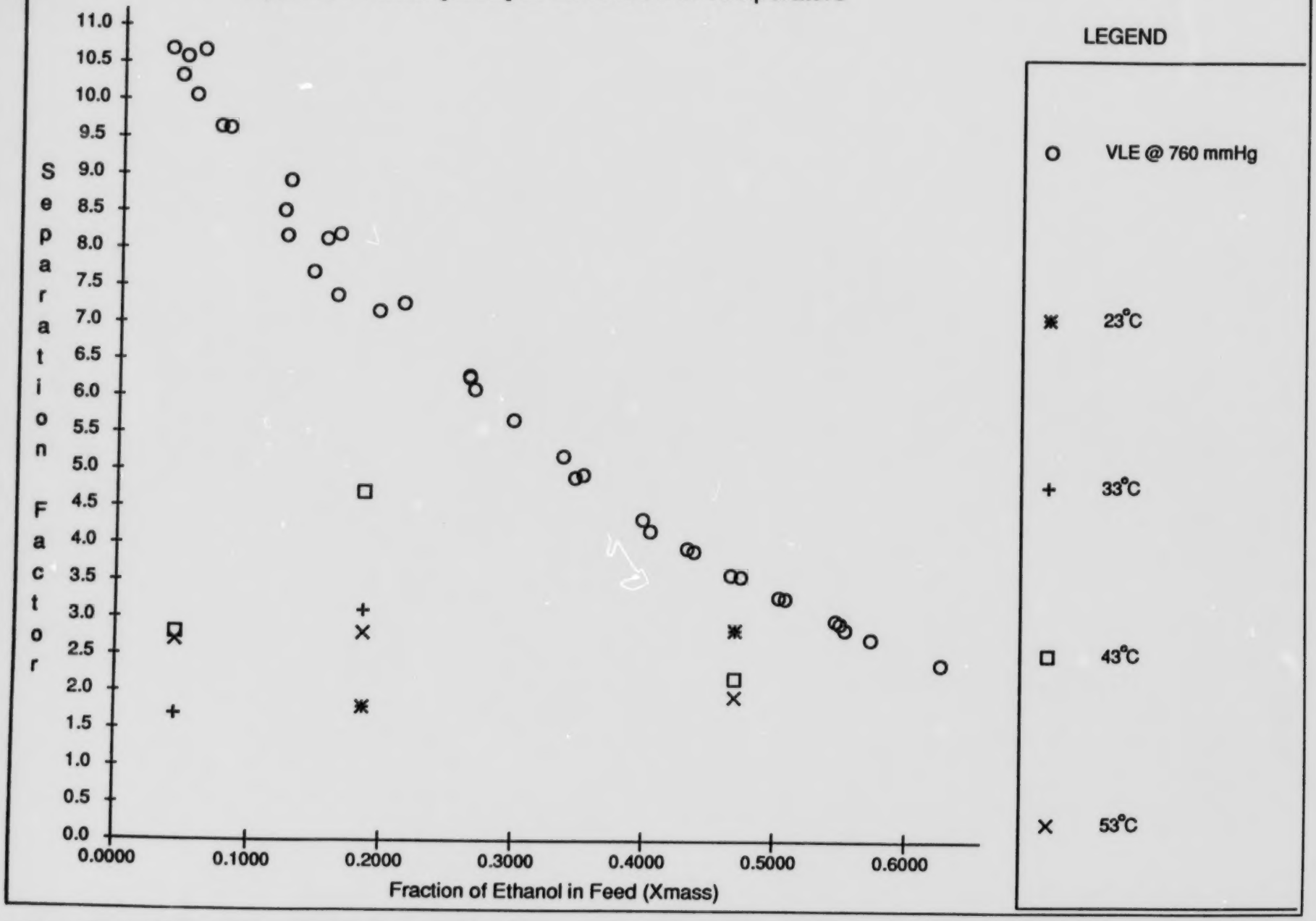
Materials that are considered hydrophilic were also found under certain circumstances to exhibit some ethanol selectivity in pervaporation. Heisler et. al. (1956) obtained some ethanol selectivity, $\alpha_{ew} = 1.1$ with 50 percent ethanol feed by the addition to the feed of a third component, in this case benzoic acid. Sheng et. al. (1986) reported cuprophan to show some minor selectivity to ethanol when the ethanol feed concentration was in the range of 20 to 50 percent. This was suggested to be a residual effect of vapour-liquid equilibrium. Similarly GFT composite membranes have also been reported in various articles (e.g. Bakish and Schnieder (1986)) to exhibit slight ethanol selectivity at low range ethanol feed concentrations. Goncalves et.al. (1983) also tested regenerated cellulose and reported selectivity to ethanol, although lower than that obtained using silicone, in the feed composition range of 10 to 70 percent.

Other materials were also observed to exhibit such behaviour, with several of note. Schissel and Orth (1984) investigated pervaporation using a variety of commercially available Thin Film Composite reverse osmosis membranes, and found some selectivity toward ethanol, particularly in the case of the FilmTec FT-30 membrane. Selectivity in the case of the FT-30 was not strong, as illustrated in Figure 4, being well below equilibrium over most of the concentration range and exhibiting an equisorptic or permeatropic point, where $\alpha_{ew} = 1.0$ (equivalent of azeotrope) near 90 percent. This membrane was also understood, however, not to be suitable for gaseous applications.

Another interesting material exhibiting ethanol selective behaviour is poly(trimethylsilylpropyne). Masuda et. al. (1986) investigated the behaviour of a group of substituted polyacetylene polymers. They found only poly(trimethylsilylpropyne) to show selectivity to ethanol, with a fairly high α_{ew} of 12 reported with a feed concentration of

Figure 4. Estimated Pervaporation Data of Schissel and Orth (1984) for FT-30 Membrane

Separation Factor [αew] as a Function of Temperature



10 percent ethanol. This was greater than equilibrium. This material was not tested in this study, although an attempt was made to obtain a sample. This material was also known to be extremely permeable and unselective in gas phase applications and is still extremely expensive. A recent Japanese Patent [60,78,601 May 05, 1985 by Sanyo Chemical Industries Ltd.] also employed poly(trimethylsilylpropyne) in a composite membrane layer on porous poly(chlorophenylacetylene), reporting an even slightly higher α_{ew} of 13 at an ethanol feed concentration of 10 percent. These two points are illustrated in Figure 5 compared with vapour-liquid equilibrium at 760 mm Hg.

Hoffman et. al. (1987) observed selectivity for ethanol using microporous Gortex PTFE with selectivity dependent on pore size, temperature and transmembrane pressure difference. Using a film with 0.45 µm pores, they found selectivities to be well below equilibrium with 0.2 µm pores they found selectivities much greater than equilibrium. The α_{ew} in this case ranged as high as 27. One final case of interest from the literature is work conducted by Smolders group in the Netherlands. By the addition of organoselective zeolite materials to a membrane, they achieved high ethanol selectivities with α_{ew}'s ranging as high as 40. This work was the basis of several approaches to achieving desired ethanol selective behaviour involving additions of specific ethanol adsorptive agents, namely organophilic zeolites and selective ethanol extractants.

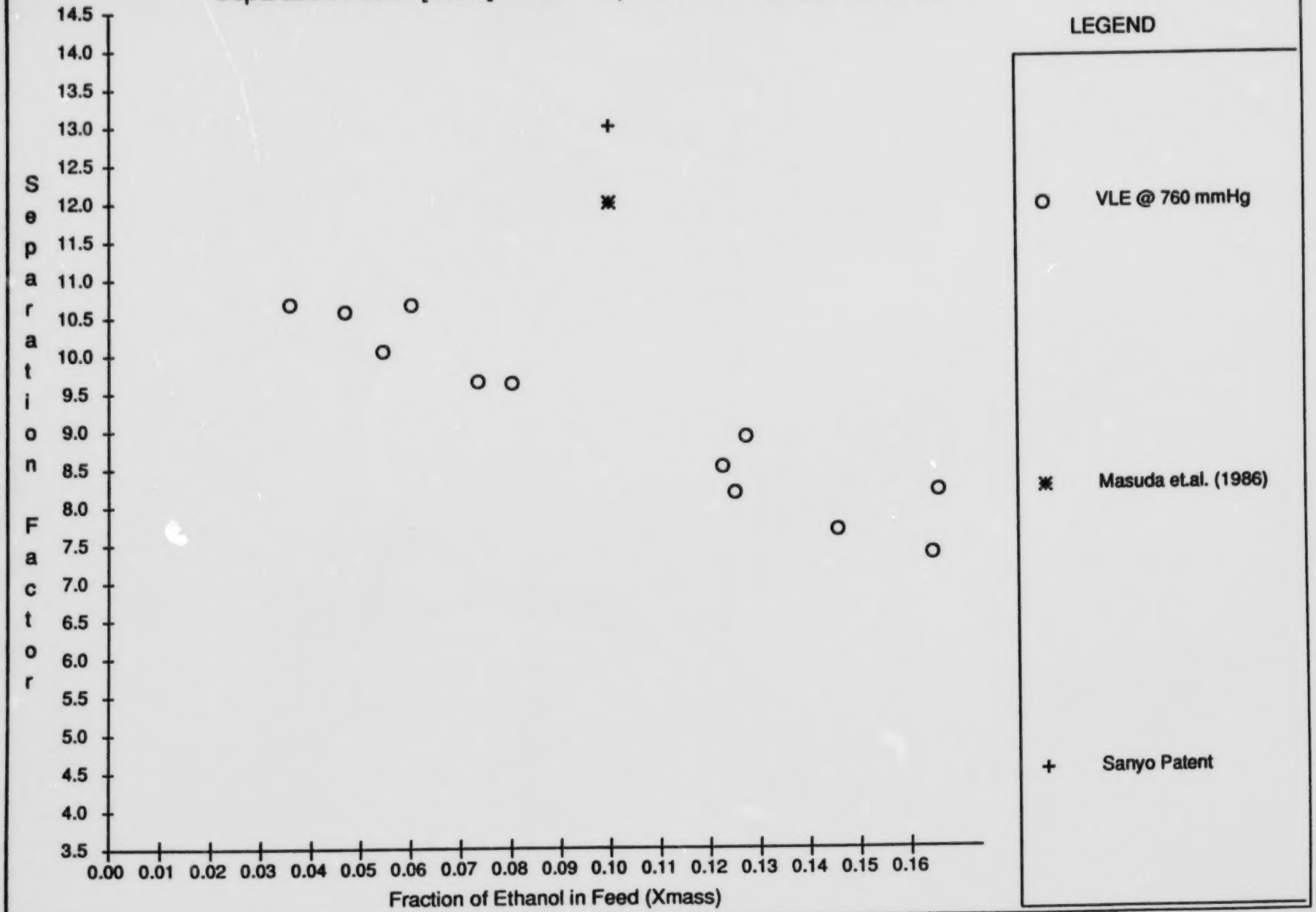
Limited information has been available from the literature regarding separations of vapours using polymeric membranes. Permeability coefficient data for various gases and vapours were presented for butadiene-acrylonitrie rubber in Rogers et al. (1972) and again in Rogers (1985). This data was interesting because it showed the permeability of methanol to be higher than water for this material. Spengler (1975) employed vapour separation in an analytical tool for trace vapour enrichment, and presented permeability coefficient data derived from Riley at UOP for silicone rubber. Extensive experimental work in the area of vapour permeation was more recently conducted by Membrane Technology and Research. In Baker et. al. (1984) vapour permeability coefficient data was presented for six different rubber materials, namely neoprene, hypalon, silicone rubber, polyvinyl chloride and nitrile rubber, using four solvents, namely octane, toluene, trichloroethane, and acetone. Condensed versions of this data were presented in Baker et. al. (1987) and Peinemann et. al. (1986). Additional work using freons was also presented in Roberts and Ching (1986). All of this data unfortunately shared the characteristic that permeability coeffients were determined at temperatures close to ambient, at low pressures, and for individual pure components.

A few other papers and references discussing vapour separations of actual mixtures were obtained with most appearing in the literature through the course of the study. In some cases, work was actually conducted at elevated temperatures as opposed to using low pressures. In almost all cases, selectivity, whether desired or otherwise, tended to be towards water.

As mentioned briefly in Leeper (1986), Monsanto is conducting research

Figure 5. Pervaporation Data for Polymer Poly(trimethylsilylpropyne)

Separation Factor [αew] Values Reported from Several Sources



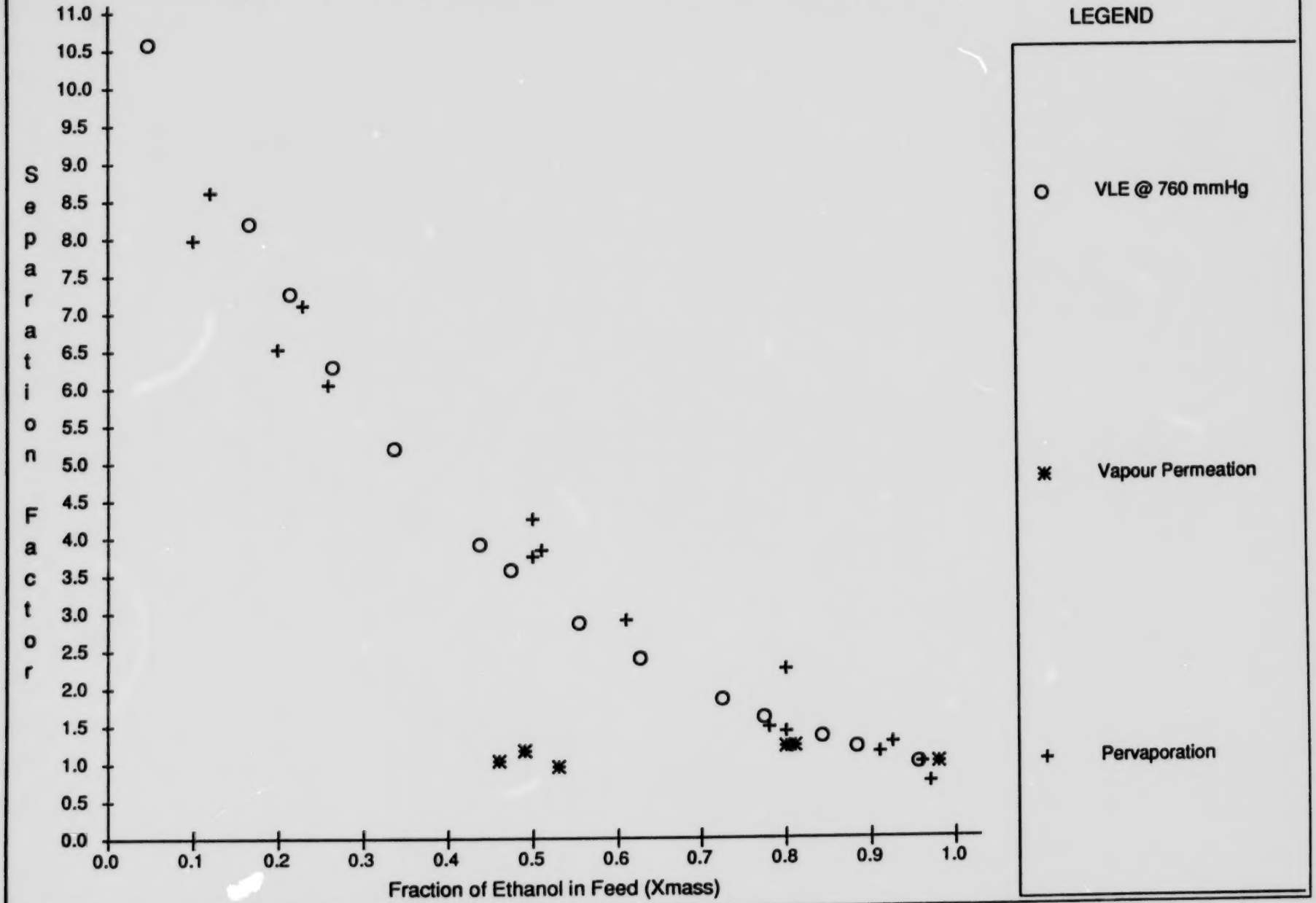
into vapour phase separation of ethanol and water with the intention of water selective dehydration. Asaeda and Du (1986) studied separation of ethanol-water mixtures using a thin selective ceramic membrane, however, in this case they were also dealing with water selectivity. Nakaura and Makino (1987) studied polyimide membranes at elevated temperatures using ethanol-water mixtures. They found this material to be water selective, and suitable for dehydration purposes.

Uragam and Saito (1987) employed vapour separation (which they termed evapomeation) at lower temperatures. For a polyalginine membrane, they obtained a similar shaped curve of selectivity as a function of concentration to that observed with the GFT PVA-PAN composite pervaporation membrane with ethanol selectivity at lower concentration ranges. This phenomenon was described in a similar manner to be an artifact of relative volatility.

Rautenbach and Meyer-Blumenroth (1987) compared pervaporation and vapour separation of propanol and found little difference. Suematsu et. al. (1987) also compared pervaporation and vapour separation but of ethanol-water mixtures using a silicone film. As indicated in Figure 6, in the range of 25°C to 70°C they found separation by vapour permeation to be very unselective with much lower separation factor results than pervaporation.

Figure 6. Estimated Pervaporation and Vapour Permeation Data of Suematsu et. al. (1987)

Separation Factor [αew] Values for Silicone at 25°C, 50°C and 70°C



5.0 EXPERIMENTAL PROCEDURES AND MATERIALS

5.1 Laboratory

All the experimental work in this study was conducted at the laboratories of the Division of Chemistry of the National Research Council of Canada, Montreal Road Campus, Ottawa, Canada, with the assistance of the Chemical Engineering Section, headed by Dr. C.E. Capes, and the Division of Chemistry, headed by Dr. D. Wiles.

5.2 Membrane Test System

Two test systems were constructed for the purposes of the study.

5.2.1 Large Cell System

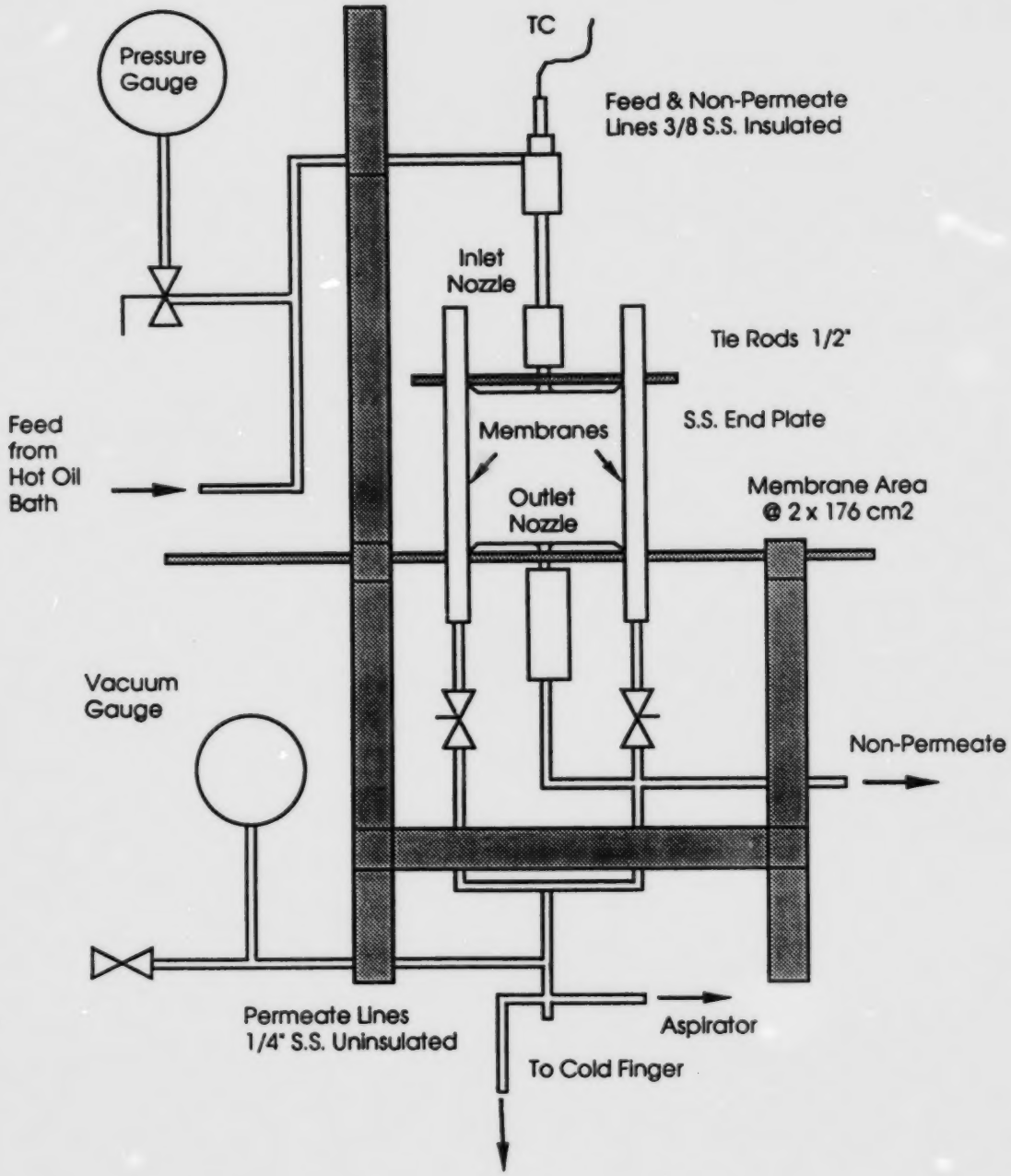
Initially, a larger cell system was constructed and employed. The rationale for this decision was that the expected flux, based on ethanol selective pervaporation data in the literature, would be very small.

A sketch of the membrane cell assembly is provided in Figure 7. The cell assembly consisted of a horizontal glass cylinder with locations for two membranes, each of approximately 176 cm^2 area, mounted vertically at either end of the cell. Feed vapour entered through a nozzle in the top of the cylinder, and non-permeating vapour exited through a nozzle at the bottom. The end plates were machined out of stainless steel, with each having a central porous stainless steel insert, and collection channels underneath. The permeate exit lines from the end plates were oriented downward so that any condensed liquids would drain out. A valve was located on each of the two permeate outlets so that either one or both of the membrane locations could be employed at any time. The total available membrane area was thus 176 or 352 cm^2 depending on whether one or two membranes were employed. Usually only one membrane was employed at a time in actual use. A compressible asbestos, PTFE covered gasket was employed on each end to seal between the plate and cylinder. A heat tape was wrapped around the glass cylinder to reduce possible condensation in the cell, and a removable, fabric enclosed Fiberfracs insulation blanket was used to cover the cell.

The general test system schematic is presented in Figure 8. The arrangement of the system was modified progressively by a series of changes with essentially the final version illustrated.

Important features of the system were as follows:

- Liquid feed vessel of 8 L capacity with stir bar.
- Double head diaphragm pump with gas bladder to dampen flow oscillations.



LARGE CELL ASSEMBLY

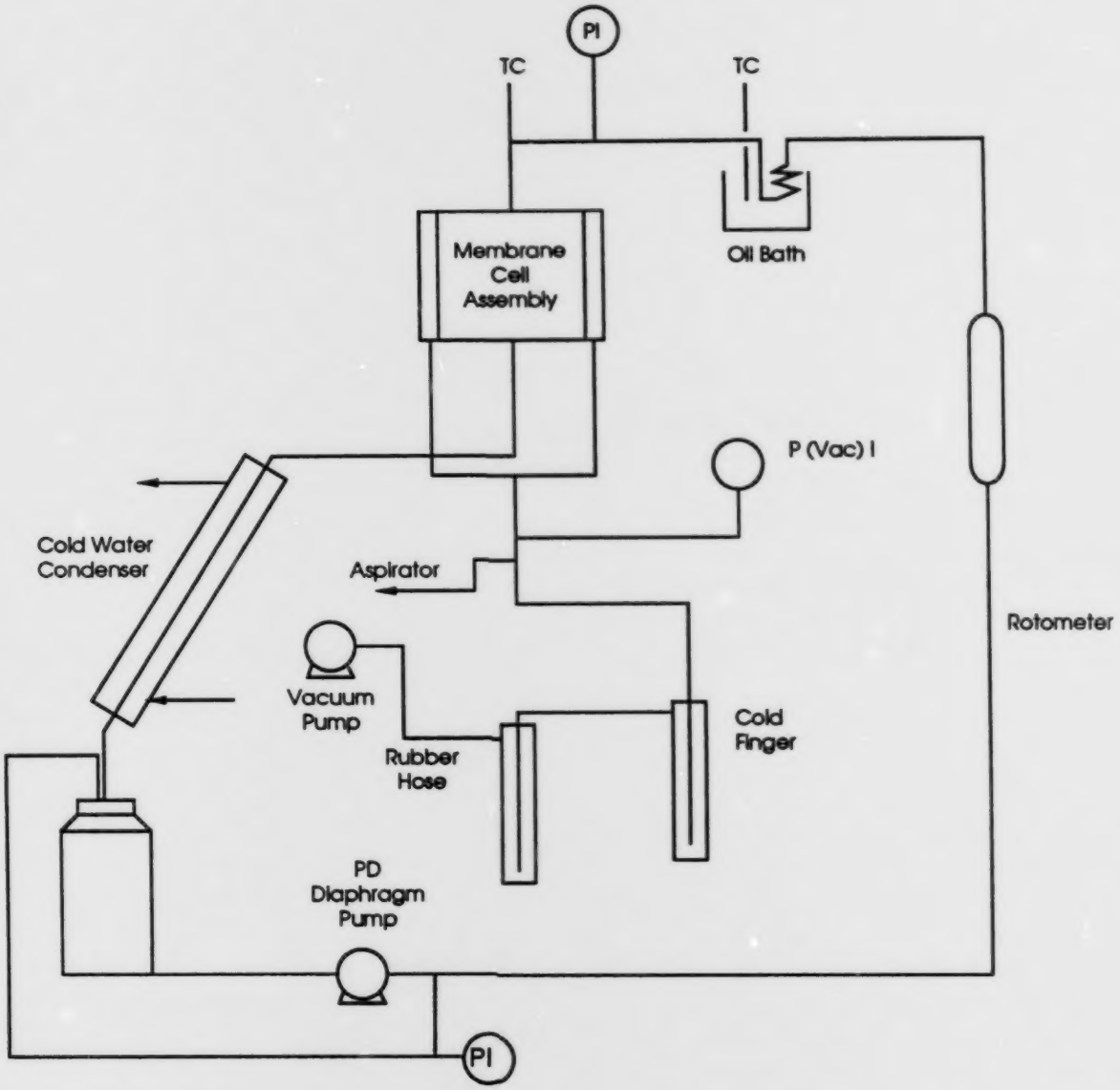
FIGURE 7

- Liquid back-pressure valve on recycle loop to control liquid feed pressure.
- Needle valve to control forward liquid feed rate.
- Rotameter to measure liquid feed rate.
- A 220 V electrically heated oil bath with feed-back temperature control system. (Note: Employed a mV setpoint to compare with bath TC output rather than a direct temperature setpoint.)
- Pressure gauge just upstream of cell to measure pressure.
- Thermocouple inserted into inlet nozzle of the cell to measure temperature in the cell.
- Valve on non-permeate outlet line from cell to control pressure in cell. Initially employed gas back-pressure valve but replaced with simple needle valve because of two-phase nature of stream.
- Recycle of condensed non-permeate back into feed tank.
- Use of a pressure gauge to measure vacuum on permeate side.
- Alternative vacuum source using a vacuum aspirator while samples not being taken so that membranes could be maintained under suction at all times. (Two-way valve to select vacuum)
- Use of two cold fingers on permeate line. Initially, the permeate collection line also included a cold water condenser, however, this was eliminated.
- First finger in dry ice/acetone or liquid nitrogen for sample collection.
- Second finger in liquid nitrogen to protect vacuum pump.

In an attempt to prevent degradation or leaching of transfer tubing, all the liquid and vapour transfer lines in the feed/non-permeate loop and all the permeate lines up to the sample trap were either metal (copper or stainless steel) glass or teflon. All metal/glass connections, such as at the cell nozzles and permeate collection tube, were made using a heat shrinkable teflon tubing sleeve with rubber tubing over top.

5.2.2 Small Modified Gas Cell

Partway through the project, a smaller gas cell was modified and installed into the test system. The use of a smaller cell was made possible/necessitated by two factors:



LARGE CELL SYSTEM SCHEMATIC DIAGRAM **FIGURE 8**

1. Vapour permeation rates were found to be quite high in the large cell so a smaller cell could be used and still achieve easily measurable permeate fluxes.

2. The use of a smaller cell allowed for much greater tolerance of membrane defects in that coupons could be selected from the best portions of cast film sheets. This had been a major impediment in the previous work with the large cell.

A standard stainless steel static cell with membrane area of 10.7 cm^2 was modified for use in thin film screening work. The cell and relevant modifications are illustrated in Figure 9, while the test system arrangement used with the small cell is presented in Figure 10. Again, as in the case of the larger cell system, a number of modifications were made through the course of the work with essentially the final version illustrated.

Salient features of the small cell and the system employed around it are summarized as follows:

- Gas cell inverted from normal position so any condensates would drain downward off the membrane.
- Inlet at bottom, outlet at top of cell cylinder near the membrane position.
- Preheating tube (10 ft x 3/8" copper) to ensure feed vapourized.
- Cell immersed directly into oil heating bath for better temperature control.
- Heating tape was wrapped around the cell permeate and non-permeate outlet lines to present condensation.
- Pressure was measured using a gauge immediately downstream of the cell on the non-permeate line.
- Temperature was measured using a thermocouple inserted into the non-permeate outlet port of the cell.
- Same feed vessel, pump, and transfer lines (feed and return) used as in larger system.
- Needle valve downstream on non-permeate return for pressure control.
- Two permeate cold traps were again employed.
- The first trap used for sample collection was much smaller, and immersed in liquid nitrogen.
- The same second trap was used as in the larger cell system to protect the vacuum pump, and allow extended operation using the vacuum pump.

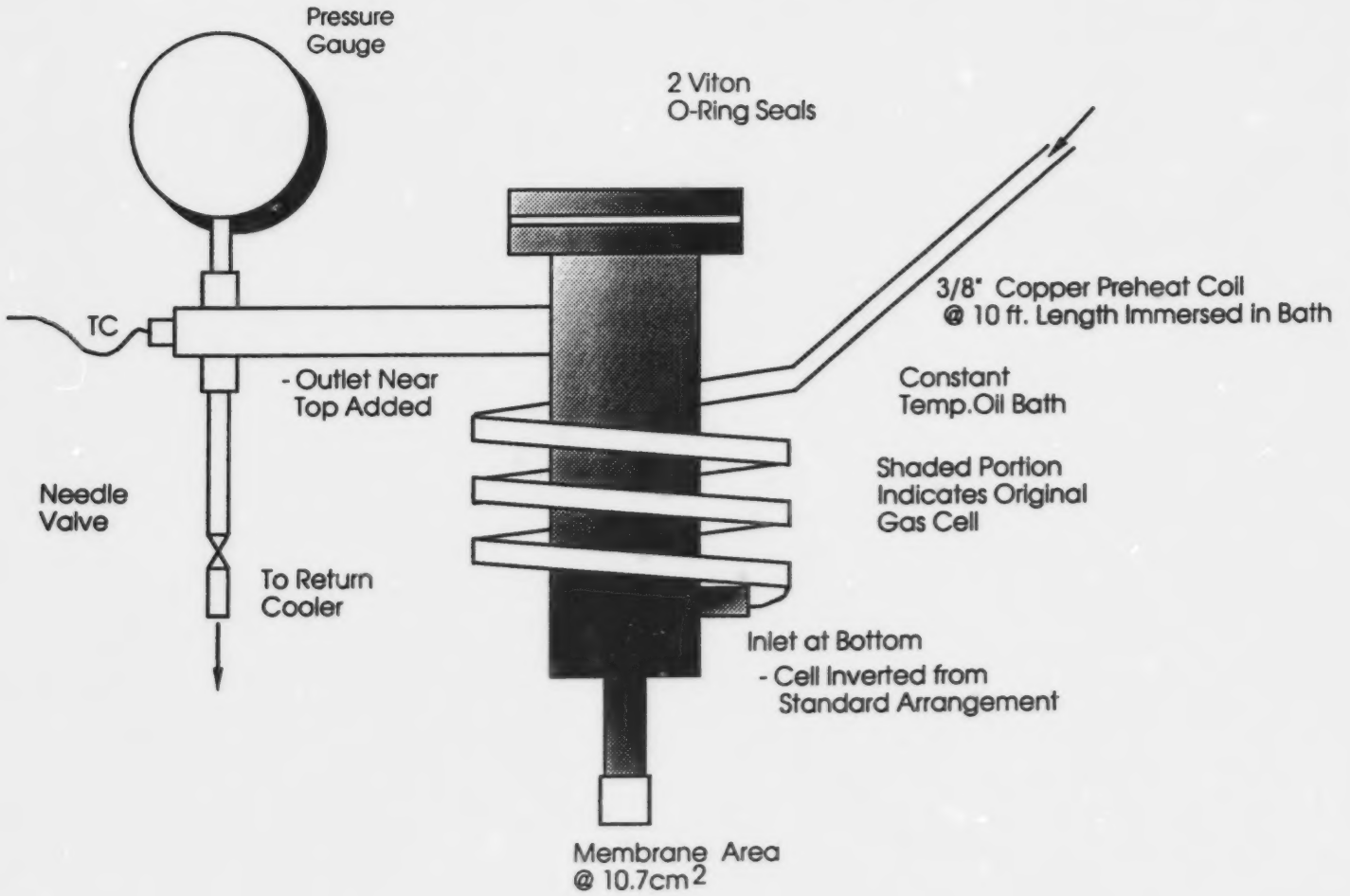


FIGURE 9

SMALL CELL ASSEMBLY

- The same arrange to allow the use of the vacuum aspirator was employed.

- Mercury manometer added for more accurate vacuum readings.

5.3 Operating Procedures

In the case of both the small and large cells, membranes were mounted in place with a filter-paper backer to ensure the membrane did not adhere to the porous stainless steel plate underneath. In the case of the small cell, a two-part silicone paste material (MDX 4-4210) was usually employed on the back side of the filter paper around the edges to form a gasket-in-place and prevent leakage into the vacuum system either through or from behind the filter paper.

In the small cell, nitrogen permeation tests were conducted at room temperature prior to actual runs in order to check the gas-tight integrity of the films, and to detect possible pinholes or other defects. A nitrogen cylinder was connected to the non-permeate outlet of the cell, and the pressure taken up to approximately 100 psig. A bubble meter was attached to the permeate outlet line at the location of the sample trap. In the case of silicone, silicone/additive and silicone-polycarbonate films, the nitrogen permeation rates were employed in conjunction with published permeability coefficient data to verify and predict effective thicknesses.

As the oil bath was heated up during start-up, membranes were usually maintained under suction with the permeate system connected to the vacuum aspirator. When the bath temperature stabilized, the feed pump system was turned on with the flow diverted to a waste vessel. Start times for runs were taken as the feed was changed into forward flow. Once forward flow was initiated, the cell temperature and pressure rose rapidly. Generally, the operating conditions stabilized within about 30 minutes. Several samples were often taken through the course of a run, with the first usually taken at one hour into the run. Run times varied between 5 hours to 16 hours.

Fluctuation in cell temperature and cell pressure was generally observed through the course of individual runs. This was often associated with fluctuation in the feed flow rate.

One of four feed compositions was employed in most of the runs, these being pure water, absolute ethanol, 50 percent ethanol and 95 percent (azeotropic) ethanol.

A temperature of 105°C was arbitrarily chosen as a target for most runs conducted. This temperature was selected as it was sufficiently above the boiling point of water to ensure that all mixed feeds would be vapourized. Actual operating temperatures generally varied between 80°C and 110°C, however, one run using a silicone film was conducted at almost 160°C. Three runs were also conducted in the small cell under vacuum conditions so that lower temperatures, in the range of 60°C to 65°C, could be employed.

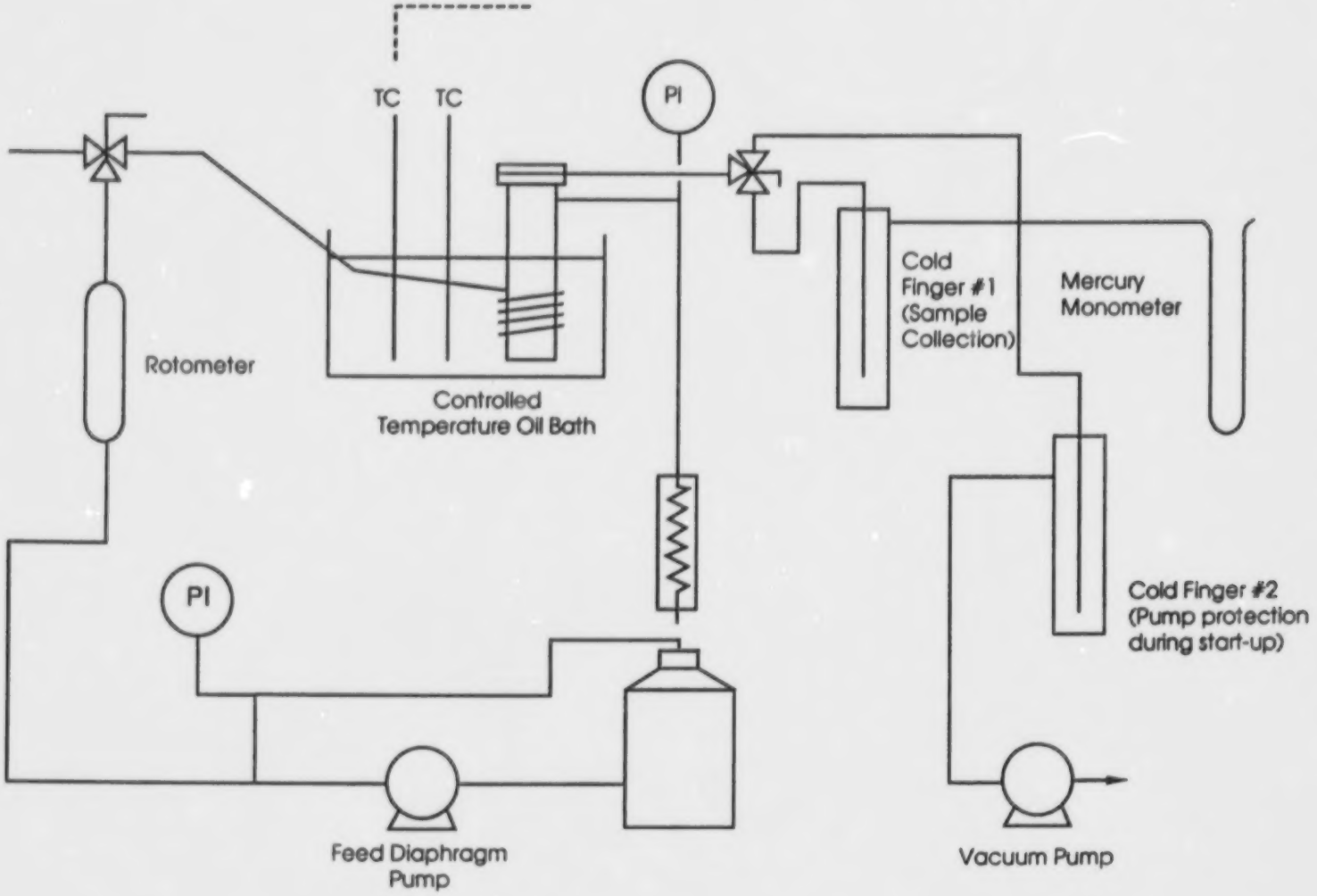


FIGURE 10

SMALL CELL SYSTEM SCHEMATIC DIAGRAM

Flux rates were determined on a mass basis by the difference in weight of permeate sample tubes before and after sampling for a specific time period of anywhere from six minutes to two hours.

During sampling, the following measurements were recorded at specific time intervals of usually one, three or five minutes:

Cell Temperature
Bath Temperature
Cell Pressure
Liquid Flow
Vacuum

Barometric pressure measurements were conducted usually prior to and after sampling.

5.4 Analytical Methods

The composition of the feed, permeate and non-permeate (retentate) samples was determined in one of two ways:

1. Refractive Index

   Compositions were determined using a Bausch and Lomb refractometer. Samples were diluted with RO purified water usually by a factor of 6:1 (5 mL of water added to 1 mL of sample) before measurement were taken. This was to avoid non-linearities existing in the relationship between refractive index and ethanol concentration at higher concentration values. Samples were measured against predetermined standards diluted in the same manner. A sample standard curve of ethanol concentration versus arbitrary refractometer measurement units is presented in Figure 11.

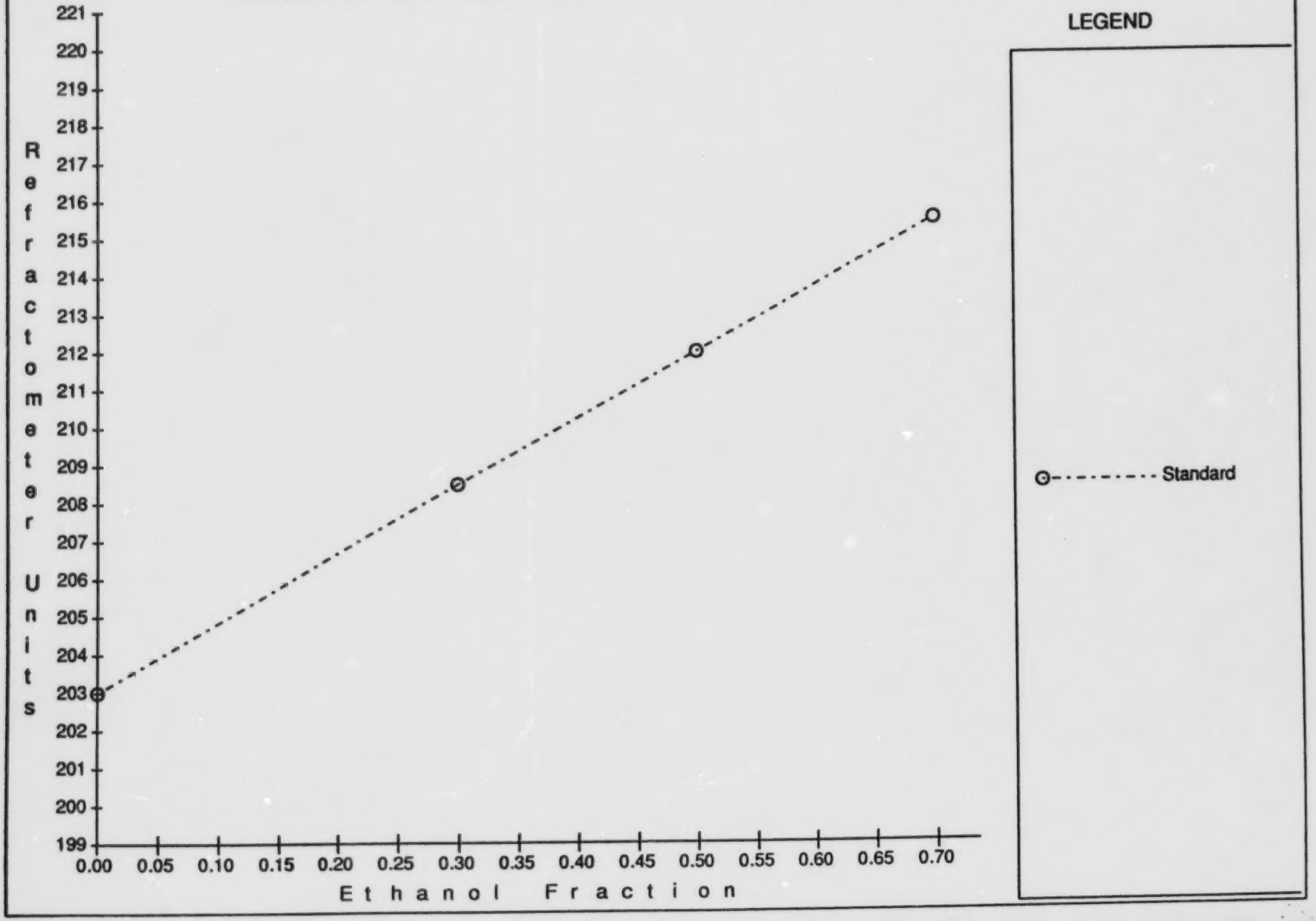
2. Gas Chromatography

   In cases where very small permeate samples were collected or when runs were performed using near azeotropic feed, the composition was determined by gas chromatography. Columns packed with Porapak T and Chromosorb 103 were used at various times. Concentrations were calculated from integrated peak areas by Normalized Area Method, as discussed in McNair and Bonelli (1968, p139), being determined for a two-component mixture as follows:

$$Conc_{(i)} = \frac{Area_{(i)} * F_{(i)}}{Area_{(i)} * F_{(i)} + Area_{(j)} * F_{(j)}}$$

The weight factor for ethanol was assumed to be equal to one (i.e. $F_e = 1.0$), and the weight factor for water (F_w) was determined from injections of known standard solutions. As illustrated in Figure 12, the weight factor for water was found to be dependent

Figure 11. Example Refractometer Standard Curve



on concentration at high ethanol concentrations.

5.5 Materials Tested

5.5.1 General Technique

A number of films and membranes were tested during the course of the study. These materials are summarized in Table 1, and are divided and discussed under five categories:

1. Rubbery Polymers
2. Other Non-Polysulfone Polymers
3. Polysulfones
4. Modified (Udel) Polysulfones
5. Specific Ethanol Selective Additives (to Silicone)

Most materials were tested as dense homogeneous films, with only a few asymmetric, high flux membranes.

5.5.2 Rubbery Polymers

1. Silicone - Polydimethylsiloxane:

Most available literature on pervaporation pointed to silicone rubber or polydimethylsiloxane as a likely candidate material to select ethanol from water. A number of silicones were employed in the course of the project, as follows:

MEM-100 - Commercial film from General Electric. Clear, 3 mil (76 µm).

MTR Comp - Composite membrane of 3.5 µm silicone on porous polysulfone backing from Membrane Technology and Research Inc.

RTV-615 - Two-part Room Temperature Vulcanization Rubber from General Electric.

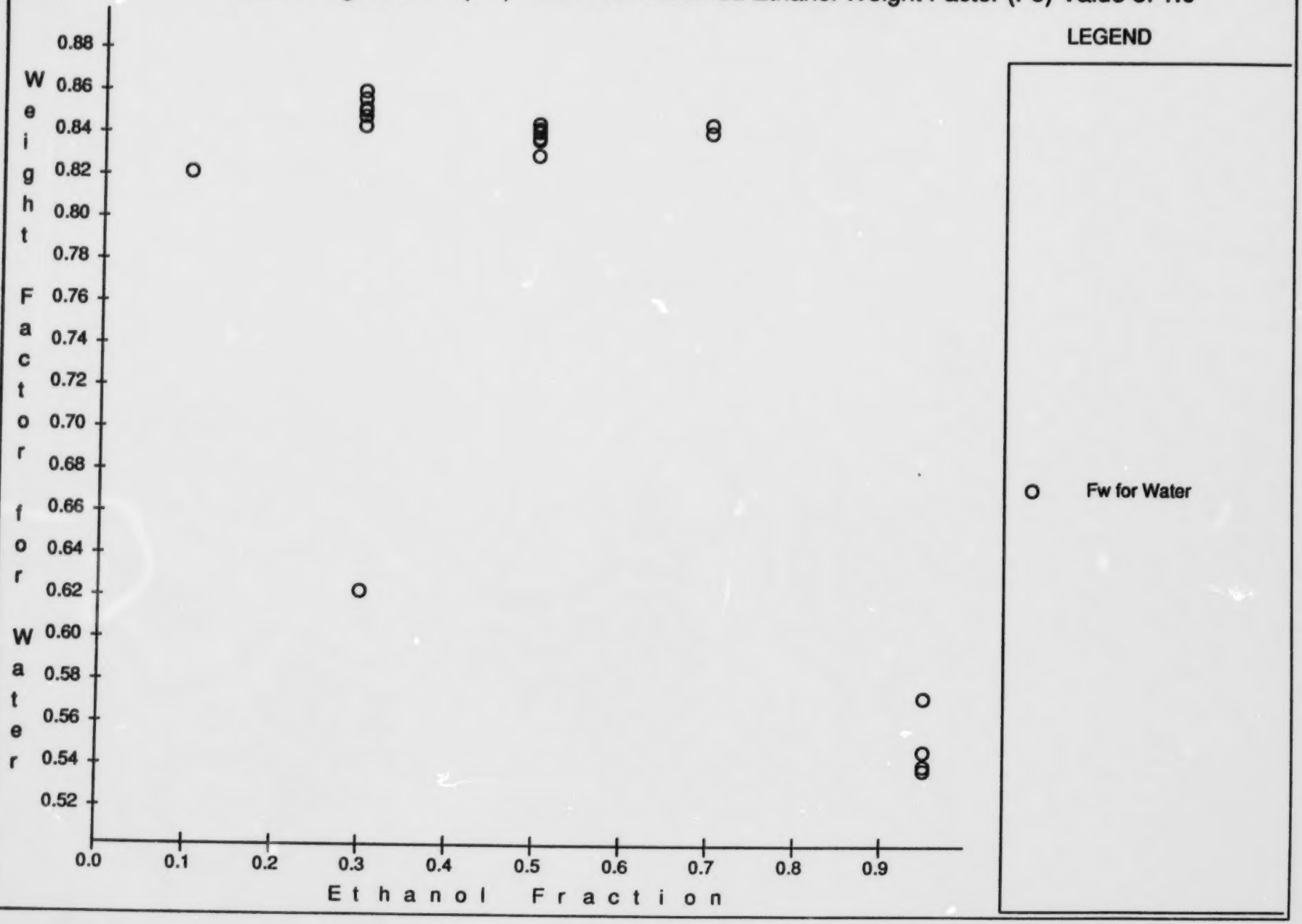
RTV-670 - Two-part Room Temperature Vulcanization Rubber from General Electric.

Silgard 184 - Two-part Room Temperature Vulcanization Rubber from Dow-Corning - platinum catalyzed.

MDX 4-4210 - Two-part Medical Grade Room Temperature Vulcanization Rubber from Dow-Corning - stanus octoate catalyzed.

Figure 12. Weight Factors for Gas Chromatographic Analysis using Chromosorb 103 Column

Water Weight Factor (Fw) Values for Assumed Ethanol Weight Factor (Fe) Value of 1.0



The two-part silicones were viscous liquid solutions prior to curing with one part of curing solution being added to 9 or 10 parts of prepolymer mix. Although these materials could be cured at room temperature (usually requiring 24 h), they were generally cured at elevated temperatures near 75°C for 30 to 40 minutes.

For tests in the small cell system, coupons of the commercial MEM-100 film were primarily employed. The MTR composite membrane and films of RTV 615 and Silgard 184 alone were run in the larger cell. RTV 615 was also mixed with selective additives as discussed later.

2. Silicone - Polycarbonate:

Coupons of the Silicone-Polycarbonate commercial film MEM-213 from General Electric were employed in both the large and small cells. The films used were of 1 mil or 76 µm thickness.

3. Neoprene W:

Neoprene (Chloroprene) was selected on the basis of results in Baker et. al. (1984), where it was indicated to be a membrane highly selective for organic vapours from air.

Neoprene W polymer was obtained from Du Pont. Polymer was dissolved to form a 15 percent solution using reagent grade chloroform, cast onto glass using a casting bar, and solvent then totally evaporated to form a film with nominal thickness of 3 mil or 76 µm. Coupons cut from the film were used in the small cell.

4. Fluorel FC-2174:

The fluoroelastomer Fluorel was selected on the basis of results in Baker et. al. (1984), where it was indicated to be a membrane highly selective for organic vapours from air.

Fluorel FC-2174 polymer was obtained from 3M. Polymer was dissolved to form solutions ranging from 35 percent to 40 percent using reagent grade methylethylketone (MEK), cast onto glass using a casting bar, and solvent then totally evaporated to form a film. One large film was used directly in the large cell without thermal treatment. A second film of 2 mil (50 µm) was cured for 10 minutes at 200°C, and cut into coupons for use in the small cell.

5. Nitrile Rubber (Butadiene-Acrylonitrile):

Nitrile rubber was selected on the basis of results in Baker et. al. (1984), where it was indicated to be a membrane highly selective for organic vapours from air, and Rogers et. al. (1972), where some pure component permeation data was published indicating a higher permeability coefficient for methanol than water.

TABLE 1

SUMMARY OF MATERIALS TESTED

Grouping	Material
Rubbery Polymers	Silicone Rubber Silicone-Polycarbonate Neoprene Fluorel Nitrile Rubber Hypalon
Other Non-Polysulphone Polymers	Polyimide Parylene "C"
Polysulfones	Udel Victrex
Modified Polysulfones	di(Trimethylsilyl) di(Butyl) di(Hydroxy) Carboxylated
Selective Additives in Silicone	Zeolites 3A S-115 Extractants Diisopropyl-L-Tartrate 1,7-Heptanediol 2-Ethyl-1, 3-hexandiol 2-Ethyl-hexanoic acid

Krynac 19.65 (19.65 percent acrylonitrile) polymer was obtained from Polysar. A thin evaporated film of about 2 mil (50 μm) thickness was made from nitrile rubber in a tetrahydrofuran (THF) solution.

6. Hypalon 20:

Hypalon, a chlorosulfonated polyethylene rubber, was selected on the basis of results in Baker et. al. (1984), where it was indicated to be a membrane highly selective for organic vapours from air. A thin film coupon was made by dissolving the polymer to 25 percent in toluene, casting onto glass and completely evaporating the solvent.

5.5.3 Other Non-Polysulfone Polymers

1. Polyimide:

Two polyimide films were made from commercial DMA solutions obtained from Northern Telecom. The first, with nominal thickness of 1.6 mil or 40 μm, was cast with a bar and subsequently reacted in an oven at progressively higher temperatures up to 250°C. The second film, with nominal thickness of 0.6 mil or 15 μm, was spun cast by Northern Telecom, and subsequently reacted in an oven at progressively higher temperatures up to 250°C. Coupons from each of these films were tested in the small cell system.

2. Parylene "C":

Parylene "C" or poly(monochloroparaxylylene) was specifically chosen to test because it has one of the lowest permeability coefficient values for water listed in the literature, as for instance in Barrie (1986). Films of 1 mil (25 μm) and 2 mil (51 μm) were obtained from Nova Tran Corporation. A coupon of 1 mil (25 μm) thickness was tested in the small cell.

5.5.4 Polysulfones

Two commercially available polysulfone resins were employed as follows:

1. Udel P3500 Polysulfone

For tests in the large cell, three different Udel polysulfone membranes and films were tested. An already made ultrafiltration membrane cast from an NMP solution and two thin dense films were employed. One of these was using a 10 percent solution of Udel in

dichloromethane and casting into an ethanol bath. The other was made from a 20 percent solution of Udel in NMP, which was filtered, cast onto glass and dried in a vacuum oven.

For coupons used in the small cell, pellets of Udel P3500 (Union Carbide) were dissolved to form a 15 percent solution using reagent grade chloroform, cast onto glass using a casting bar, and solvent then totally evaporated to form a film with nominal thickness of 2 mil or 50 µm. Sample strips cut from this film sheet were boiled in ethanol to verify that all solvent had been evaporated. Coupons cut from the film were used in the small cell.

2. Victrex Polysulfone

Victrex Polysulfone (ICI) powder was dissolved to form a 15 percent solution using reagent grade chloroform. The polymer did not dissolve well in this solvent, forming effectively a two-phase mixture. The solution was nevertheless cast onto glass using a casting bar, and solvent then totally evaporated. A coupon of 2.8 mil or 71 µm nominal thickness was obtained from this film, and tested in the small cell.

Attempts were also undertaken to make suitable films of Radel polysulfone, however, this material was not tested.

5.5.5 Modified Polysulfones

One of the major motivations for working at NRC was to take advantage of recently developed, specifically modified Udel polysulfones. These polymers and the method of their preparation are discussed in Guiver et. al. (1986) and Guiver et. al. (1988). Several modified polysulfone materials were tested as follows:

Functional Group Added	Equivalent Substitutions per Repeat Unit	Nature of Polymer
Trimethylsilyl	2.00	Hydrophobic
Butyl	2.00	Hydrophobic
Hydroxyl	2.00	Hydrophilic
Carboxyl	0.25	Hydrophilic
	0.40	
	0.60	
	0.63	

These modified polysulfone compounds, their manufacture and uses constitute an ongoing research project at the National Research Council of Canada, Ottawa, Canada, and patent protection is being sought by NRCC for the results of this work. Any enquiries regarding research into modified polysulfones at the National Research Council of Canada should be directed to Dr. C.E. Capes, Head, Chemical Engineering, Division of Chemistry, National Research Council of Canada, Ottawa.

Dense films were made from all these materials and tested in the small cell. Asymmetric membranes were also made from the hydrophobic di(trimethylsilyl) and di(butyl) versions and tested in the large cell. The individual materials are discussed as follows:

1. Di(trimethylsilyl) Udel Polysulfone

   Asymmetric type membranes were made of di(trimethylsilyl) modified Udel polysulfone by dissolving reprecipitated polymer to 20 percent in a DMA solution, casting onto glass using a 10 mil (250 µm) casting bar, and immersing into baths of both water and ethanol. Dye testing was performed on these membranes to check for pinholes, which showed numerous penetration points. Membranes were nevertheless tested in the large cell system.

   Dense film coupons were made from recovered di(trimethylsilyl) Udel dissolved to 20 percent in a solution of reagent grade chloroform. This solution was cast onto glass, and the solvent completely evaporated to produce a clear film. A coupon of 2.4 mil or 61 µm cut from the film was tested in the small cell system.

2. Di(butyl) Udel Polysulfone

   Asymmetric type membranes were made of di(butyl) modified Udel polysulfone by dissolving reprecipitated polymer to 20 percent in a DMA solution, casting onto glass using a 10 mil (250 µm) casting bar, and immersing into baths of both water and ethanol. Dye testing was performed on these membranes to check for pinholes, which showed these films to be largely defect free. Membranes were tested in the large cell system.

   Dense film coupons were made from fresh reprecipitated di(butyl) Udel dissolved to 20 percent in a solution of reagent grade chloroform. This solution was cast onto glass, and the solvent completely evaporated to produce a clear film. A coupon of 2 mil or 50 µm cut from the film was tested in the small cell system. In an attempt to test possible protection of the polysulfone from direct vapour attack, a di(butyl) coupon was laminated with RTV 615 silicone. This film was of roughly 175 µm thickness: 50 µm polysulfone plus 125 µm silicone.

3. Di(hydroxy) Udel Polysulfone

   Dense film coupons were made from di(hydroxy) Udel dissolved to 20 percent in a solution of reagent grade chloroform. This solution was cast onto glass, and the solvent completely evaporated to produce a clear film. A coupon of 2 mil or 50 µm cut from the film was tested in the small cell system.

4. Carboxylated Udel Polysulfone

   Both dense and porous asymmetric films of carboxylated polysulfone

were tested, all in the small cell. Because this polymer exhibited poorer solubility in chlorinated solvents, the films were all made using either DMA or NMP as solvent.

Several carboxylated PSf coupons were obtained from M. Guiver of NRC as follows:

Membrane	Description
MG300-B4-4 MG300-B4-2	Dense surface layer films cast from 20 percent solution of 0.25 equivalent carboxylated polymer in DMA.
OKNMP-84-4	Porous membrane cast from solution of 0.4 equivalent carboxylated polymer in NMP.
G2-5-4 G2-5-1	Porous membranes cast from solution of 0.63 equivalent polymer in DMA solution.

Coupons were also made from 0.6 equivalent substitution carboxylated Udel polymer also supplied by M. Guiver of NRC. The polymer, in salt form, was soaked in dilute HCl, then dissolved in an NMP solution, reprecipitated and dried. Two solutions in DMA solvent were prepared using the purified material as follows:

A Solution: 25 percent by weight 0.6 carb PSf in reagent grade DMA.

B Solution: 25 percent total polymer solution in reagent grade DMA. A polymer mix was used of one half by weight each of 0.6 carb PSf and Victrex PSf.

Membranes were cast from each solution onto two consecutive glass plates in series using a 12 mil casting knife. The plates were dried in an enclosed oven at 80°C to form a skin layer for the following times:

A1 and B1 for 10 minutes
A2 and B2 for 15 minutes

Membranes were then immersed into ice-chilled water baths and soaked overnight prior to cutting into coupons. Optical microscope examination, corroborated by nitrogen permeation tests, showed these films to all have thick surface layers.

5.5.6 Selective Additives in Silicone

Two approaches to obtaining an ethanol selective membrane were investigated, which involved agents with specific affinity for ethanol. Both of these approaches were based on work in pervaporation membranes conducted by Smolder's group in the Netherlands. The central concept was the incorporation of selectively adsorbing materials in a matrix of

silicone, which is less selective but provides for binding and sealing for gas tightness.

1. Zeolites:

The use of zeolites as selective adsorbents borrowed directly from work by Smolders group. As described in, for instance, te Hennepe et. al. (1987), they incorporated zeolites in silicone films for pervaporation, and achieved significant α_{ew} separation factors near 40.

Zeolites, as described in Breck ( ), are crystalline alumino-silicates with highly uniform structures and resulting highly uniform "pore" openings, which can exert selective "molecular sieving" on the basis of molecular size and also by adsorption. Most standard commercial zeolites will adsorb water. By selecting a proper opening size to exclude ethanol, they can be used to dehydrate ethanol mixtures. Such commercial processes are already available and are described for instance in Garg and Yon (1986).

Aside from the more usual zeolites, which are hydrophilic, there are also so called "hydrophobic" zeolites, such as silicalite described in Flanigen et. al. (1978), which have high silica content and will selectively adsorb organics including ethanol from water. The adsorptive separation characteristics of silicalite for ethanol/water vapour mixtures are discussed in Klein and Abraham (1983).

Two types of fine powdered zeolite molecular sieves were obtained from Union Carbide as follows:

1. Type 3A zeolite with 3Å dimension openings - water selective.
2. Type S-115 silicalite with 6Å openings - organic selective.

A number of silicone zeolite films were made using both of these materials and tested in the small cell system.

Zeolite was mixed in an appropriate weight proportion with the two-part liquid silicone RTV 615. Two mixture proportions were used, being 1/3 and 2/3 by weight of zeolite. In order to achieve more thorough mixing of this viscous mixture, volatile solvent was then added to a level of approximately 1/3 of the total weight. The molecular size of the solvent in each case was chosen to be larger than the zeolite aperture and so as thus not readily adsorbed. Freon (trifluorotrichloroethylene) and hexane were used in the case of 3A zeolite, while cyclohexane and isooctane were used in the case of silicalite. Films were cast onto glass using a glass rod, and placed in a sealed oven to drive of solvent. Because of the highly porous nature of the zeolite materials to gases, a thin sealing layer of silicone was first laid down on the glass in the case of 2/3 zeolite films.

2. Ethanol Extractants:

The second approach to selectivity was to investigate chemical species that would have specific ethanol affinity. It was intended that these materials be used for direct incorporation within a silicone or other film as in the case with the zeolites, or, alternately, for identification of appropriate functionality for membrane polymers.

In this regard, the assistance of Professor A. Daugulis' group at Queen's University was obtained in trying to identify potential candidate chemicals. Professor Daugulis' group had done extensive work identifying ethanol selective liquid solvents for the development of extractive (liquid-liquid) fermentation systems as described in Kollerup and Daugulis (1985). In the process they assembled a large database of more than 1,500 potential candidate extractants.

Although there are obvious differences between liquid-liquid extraction and vapour permeation processes, certain similarities can be drawn with both involving selective partitioning that are especially important given that one of the proposed mechanisms of vapour transport within membranes involves capillary condensation, as mentioned for instance in Asaeda and Du (1986).

Ranking criteria and initial process conditions were selected for the selection program and a list of candidate chemicals was generated. The ranking was conducted at a temperature of 40°C, a pressure of 2 atm, and with an initial composition of 45 percent water, 45 percent ethanol and 10 percent extractant. Unfortunately higher temperatures, closer to actual process conditions, could not be attempted because the program necessitated that all solvents in the database be in the liquid phase. The results were based solely on ranking by α_{ew} separation factors, and indicated the following general ranking of compounds: alcohols > esters > alkanes/alkenes/ aromatics. Halogenation appeared to have little systematic effect with halogenated compounds spread fairly uniformly throughout the list.

The top ten compounds from the ranking are listed as follows:

	Compound	M.W.	Density	B.P.(°C)
*	Diisopropyl L-tartrate	234.25	1.114	152 @ 12 mm Hg
	Dibutyl L-tartrate			
	1,6-Hexanedial			
*	1,7-Heptanediol	132.20	0.951	259
	7-Octene-1,2-diol			
*	2-Ethyl-1, 3-hexanediol	146.23	0.933	241-9
	3,4-diethyl-3,4-hexanediol			
	Hydroxycitronnellal			
	Dichloroacetaldehyde			

Most of the top ten compounds were di-functional, usually a di-alcohol functionality where the hydroxyl groups were or could be in close proximity. The three compounds marked with an asterisk (*), diisopropyl L-tartrate, 1,7-heptanediol and 2-ethyl-1,3-hexanediol, were chosen for testing in the small cell system. These three compounds all had di-alcohol functions and rather high boiling points, such that it was unlikely they would be lost from the membrane.

Membranes incorporating these materials were made in much the same manner as those for zeolites. Extractants were mixed with the two-part liquid silicone RTV 615, in a weight proportion of 1/3 extractant to 2/3 silicone. No dilutants were added in this case, however, silicone sealing layers were used, as in the case of zeolites.

Aside from the three extractants run in tests in the small cell, the extractant ethyl hexanoic acid was mixed in silicone to a proportion of 10 percent by weight and the film tested in the large cell system.

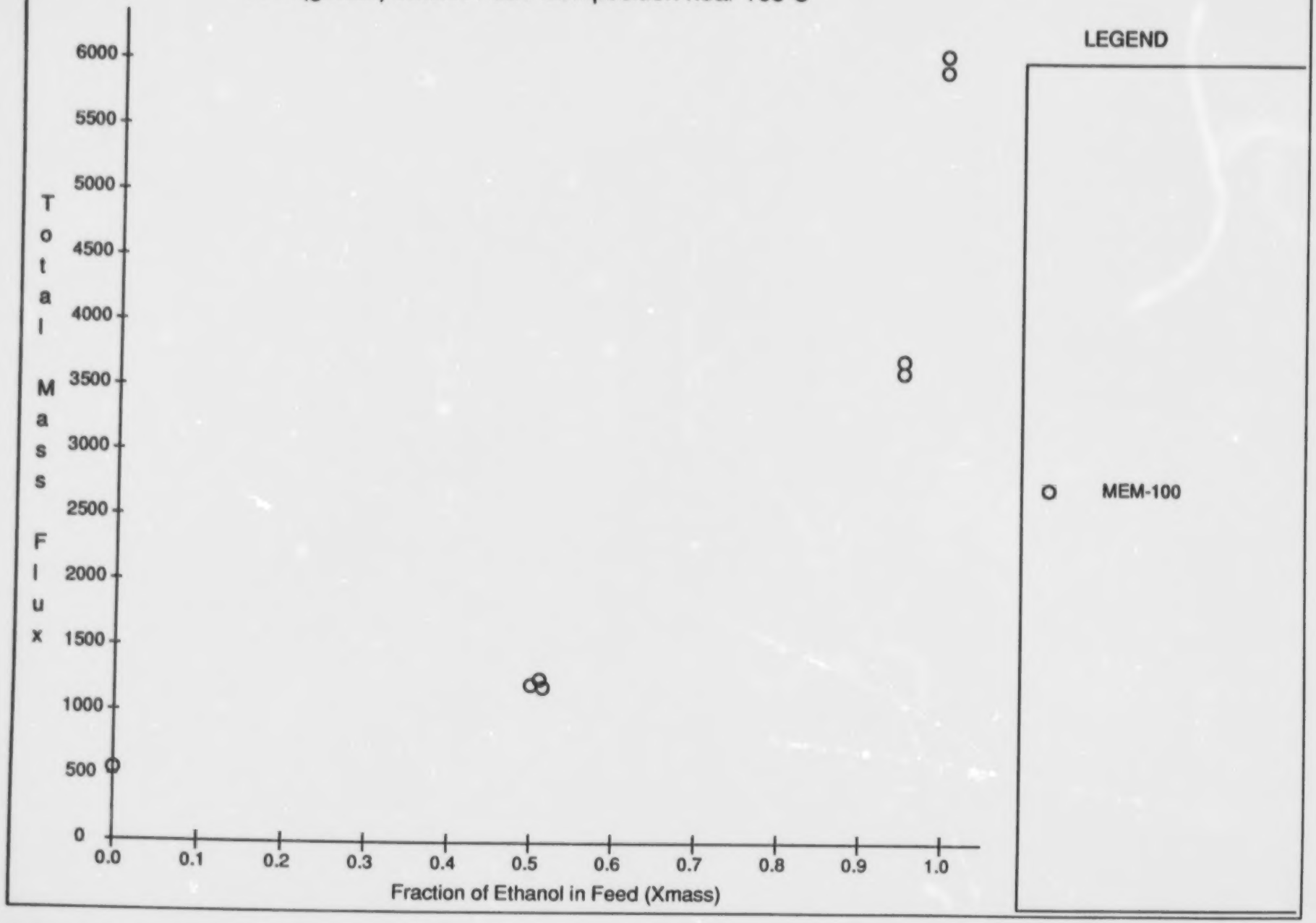
3. Vacuum Operation at Lower Temperature:

During three runs, the outlet line from the cell after the back-pressure needle valve was connected to the vacuum aspirator system. This was done in order to run the feed side of the cell under vacuum and thus allow for operation with vapour in the cell at lower temperatures.

Three films were tested under these conditions, being silicone MEM-100, and RTV 615 silicone films incorporating extractant ethyl hexanediol and the zeolite S-115 silicalite.

Figure 13. Total Membrane Mass Flux for MEM-100 Silicone Film

Flux (g/m2h) versus Feed Composition near 105 C



6.0 RESULTS

The results of materials are discussed in the same order as materials were presented in the Experimental Section.

6.1 Rubbery Polymers

6.1.1 Silicone (Polydimethylsiloxane)

In the small cell system, an extensive set of runs were conducted using a 3 mil (75 μm) coupon of General Electric MEM-100 polydimethylsiloxane film. Four different feed compositions were employed: pure water; absolute ethanol (99.5 percent); 50 percent ethanol mixtures; and azeotropic ethanol (95 percent).

Room temperature nitrogen permeation tests were conducted on the coupon through the course of the runs. Measured permeation rates varied from about 0.67 to 0.75 mL/min. These rates predicted film thickness of almost 50 percent higher than that specified, however, the permeation rates did not change significantly through the course of the runs. This consistency indicated that the polymer was not adversely effected.

Total mass fluxes obtained for the different feed mixtures at temperatures near 105°C are illustrated in Figure 13. There was a fairly large difference in pure component mass fluxes, with the ratio of pure ethanol to pure water flux of more than ten. The pressure in the cell at this temperature was of course much higher in the case of ethanol (ca 19 psi for ethanol versus ca 3 psi for water) due to its greater volatility. The α_{ew}^* ratio of estimated pure component Permeability coefficients, which is effectively molar based and also discounts membrane pressure differences, was only 2.4 at this temperature.

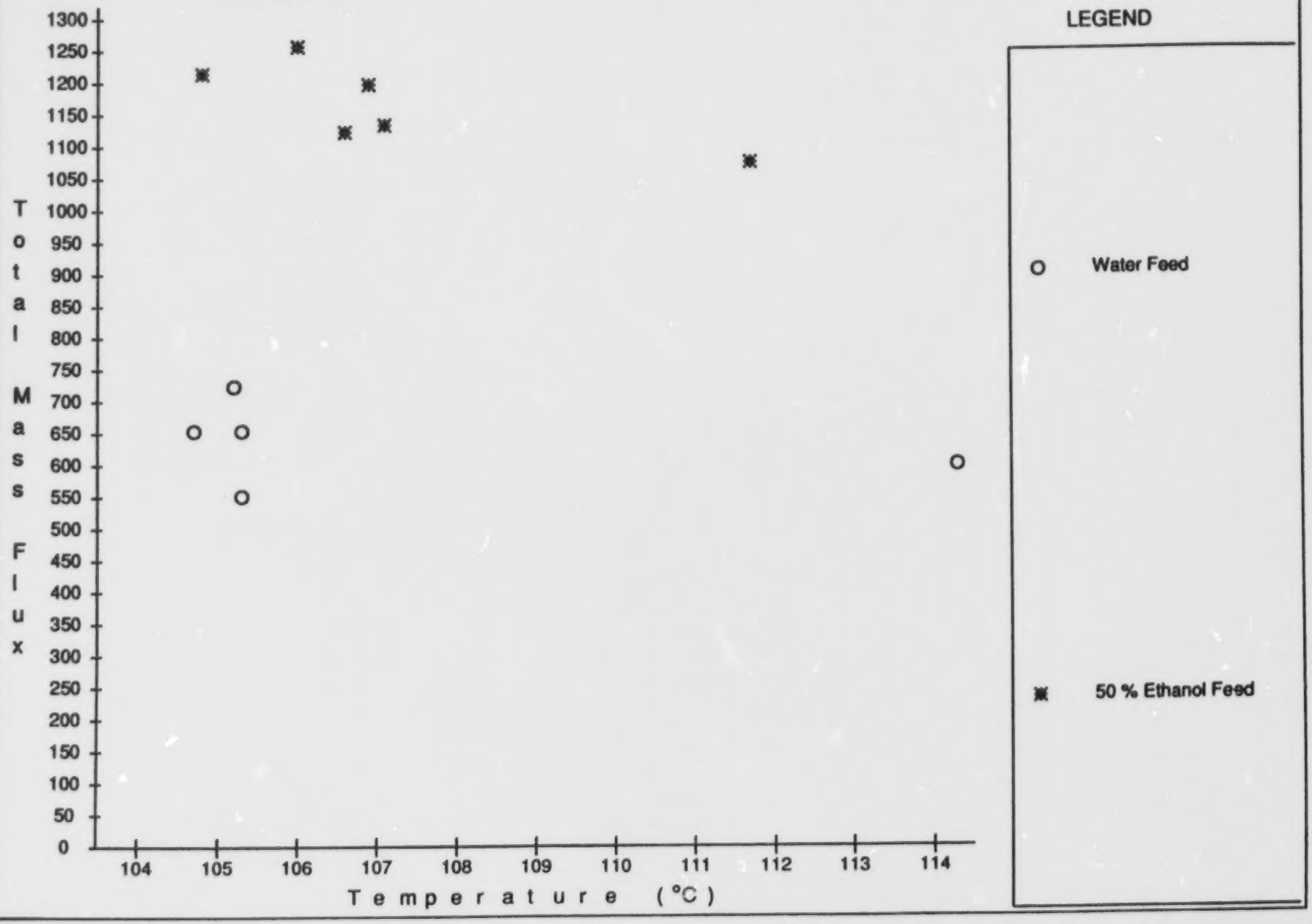
Pure component fluxes were also compared at equivalent cell pressures (ca 3 psi at ca 105°C for water and ca 83°C for ethanol). On this basis, the ratio of pure ethanol to pure water mass flux was only about six.

If the α_{ew}^* ratio is used as a guide to indicate potential separation, as it is employed in the case of conventional gas separations, then, ignoring inherent non-idealities, the results at 105°C indicated potential but low selectivity to ethanol by silicone. This result does run somewhat contrary to Permeability coefficients reported in Baker et. al. (1987) where ethanol was consistently found to be lower than water. Their results were produced using low vacuum to generate vapours as opposed to higher temperatures.

Variations of membrane flux with temperature for pure water, 50 percent and 95 percent (azeotropic) ethanol mixtures, and absolute ethanol are presented in Figure 14 and Figure 15. In the case of absolute and

Figure 14. Total Membrane Flux for MEM-100 as a Function of Temperature

Flux (g/m2h) for Pure Water and 50% Ethanol Feed Mixtures



95 percent ethanol the total flux appeared to increase with temperature as is normally expected in conventional gas separation, while in the case of pure water and 50 percent ethanol feeds, the total flux appeared to decline somewhat with temperature.

In terms of separation, no differences (within experimental errors) were observed between feed and permeate sample ethanol concentrations at all temperatures tested when 95 percent (azeotropic) ethanol feed was used. This indicated virtually no selectivity of the silicone film (or $\alpha_{ew} = 1$).

Quite different behaviour was observed when the feed composition was near 50 percent ethanol. The separation factor, α_{ew}, as illustrated in Figure 16, declined with increasing temperature, crossing over from ethanol selectivity to water selectivity within the range observed. The finding of a change from ethanol to water selectivity with a "permeatropic" or "equisorptic" point, where $\alpha_{ew} = 1.0$, as the temperature increased, was unexpected.

Several runs were conducted with the larger cell system using RTV 615, Silgard 184, and a composite thin film silicone on polysulfone membrane obtained from Membrane Technology and Research. In all these cases, feed compositions near 50 percent ethanol were used. A comparison of permeation fluxes obtained using the RTV 615 film with those obtained in the small cell using MEM-100 is presented in Figure 17.

The total permeate fluxes obtained using the RTV 615 film were about half those obtained in the small cell using the MEM-100 film. Given in general that flux is inversely proportional to membrane thickness, these results seemed reasonable since the measured thickness of the RTV 615 film (130 µm) was roughly twice that of the MEM-100 (75 µm). In both these cases, total fluxes tended to decrease slightly with increasing temperature.

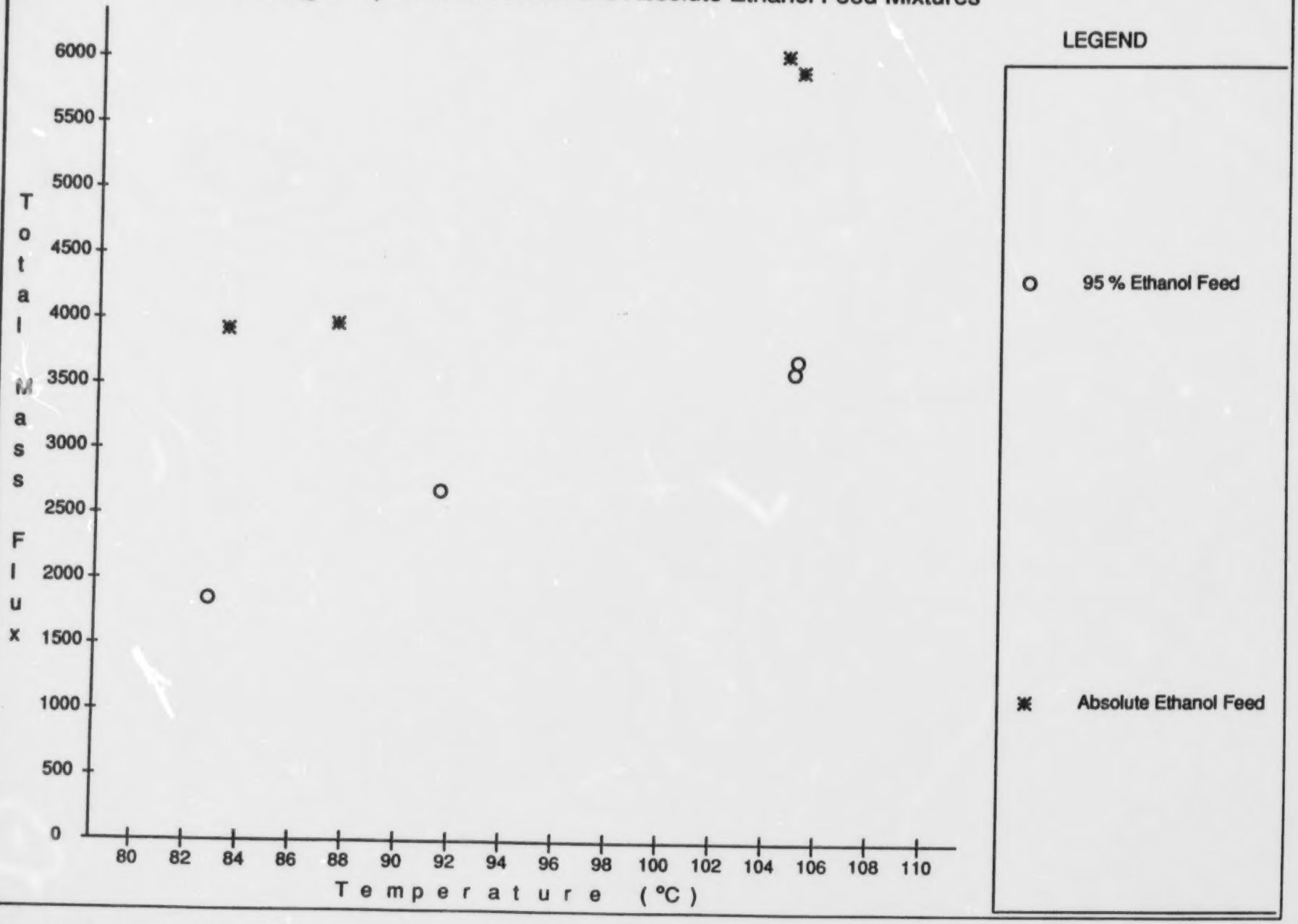
The total flux valves obtained with the MTR composite membrane are presented in Figure 18 as a function of temperature. The total flux was of a proper order of magnitude relative to the other silicone films given the provided thickness of the silicone layer (3.5 µm).

A summary plot of α_{ew} as a function of temperature for all films tested in the large system, as well as runs in the small cell using MEM-100 is presented in Figure 19. The definite general trend of declining separation factor with temperature and a cross-over in selectivity was still apparent.

The flux and separation characteristics of the MTR composite membrane suggested that the surface silicone coating was controlling the permeation, and that the porous polysulfone support played little role in determining the performance of the membrane in this system. It is very important, however, to note that this silicone coated polysulfone membrane survived exposure to the high temperature, solvent vapour ethanol containing environment intact, while dense and asymmetric films and membranes of Udel polysulfone alone were destroyed by such exposure, as discussed in a later portion of the Results section.

Figure 15. Total Membrane Flux for MEM-100 as a Function of Temperature

Flux (g/m2h) for 95% Ethanol and Absolute Ethanol Feed Mixtures



The results achieved with silicone films and coated membranes were intriguing. The selectivity of the polymer showed an obvious dependence on temperature with the apparent ability to change from being ethanol selective to water selective exhibited by increasing the operating temperature. As mentioned in an earlier section, the temperature dependence of the αew separation factor can be described by an Arhenius relationship, as follows:

$$\alpha_{ew} = k_1 \, e^{-(k_2/RT)}$$

where k_1 and k_2 are constants

Based on all the data points for MEM-100, RTV 615 and the MTR composite membrane, the values of the constants for silicone rubber were estimated as follows:

$$k_1 = 7.8 \times 10^{-3}$$

$$k_2 = 8.1 \times 10^{3} \text{ J/mol}$$

Silicone was never, however, found to be very selective one way or another. In all runs conducted using feed compositions near 50 percent, the maximum and minimum permeate concentrations obtained were approximately 60 and 40 percent respectively.

From the point of view of seeking an ethanol selective membrane, the results were a disappointment. The best selectivity achieved using 50 percent ethanol feed mixtures was an α_{ew} of approximately 1.5, and this was well below corresponding Relative Volatility, approximately equal to 3.0 for a 50 percent liquid mixture at 760 mm Hg. No selectivity was found when using 95 percent (azeotropic) ethanol feed. While these results were poor, they represented the best selectivity to ethanol achieved in the entire study.

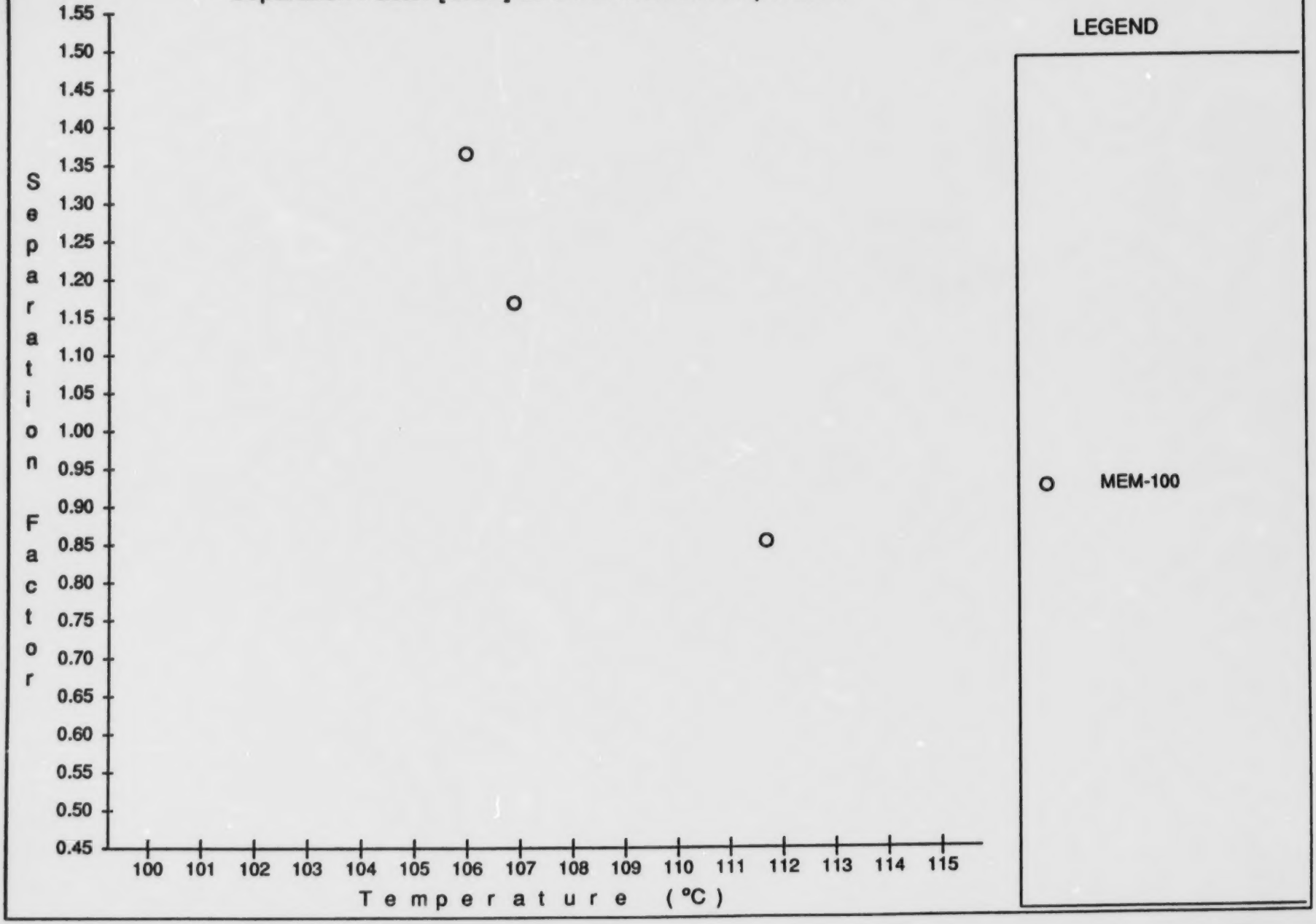
6.1.2 Silicone-Polycarbonate

A coupon of the commercial MEM-213 film from General Electric was tested in the small cell using pure water, 50 percent ethanol mixtures and absolute ethanol as feed.

Prior to any test runs, a room temperature nitrogen permeation was conducted on the coupon, with a measured permeation flux of 0.97 mL/min. From this value a nitrogen permeability coefficient value of 7.3×10^{-9} $(cm^3 \, cm)/(cm^2 \, s \, cmHg)$ was calculated, which compared well to the value listed in literature by General Electric of 7×10^{-9} Nitrogen permeation decreased slightly after test runs, but did not change in a progressive or systematic manner in proportion to accumulated exposure to vapours, indicating that the polymer was not adversely affected.

The total mass fluxes obtained for the silicone-polycarbonate film at

Figure 16. Selectivity of MEM-100 Silicone for Ethanol as a Function of Temperature



various feed compositions near 105°C are presented in Figure 20 along with values obtained using the MEM-100 silicone film for comparison.

While the actual total flux values for the silicone-polycarbonate were slightly higher than silicone because a thinner film was employed, the ratios of pure component fluxes and permeability coefficients were slightly smaller than silicone as follows:

Ratio (EtOH/Water)	Silicone	MEM-213
Mass Flux	11	10
Molar Flux	4.3	3.9
Permeability Coefficient	2.4	2.0

Based on the pure component fluxes, fairly comparable behaviour to silicone was expected for the separation of 50 percent ethanol feed mixtures. The results were surprisingly different, as illustrated in Figure 21. The silicone-polycarbonate consistently showed slight water selectivity in a similar temperature range, with α_{ew} being fairly constant near 0.6. This result was even more surprising given that a run was conducted earlier using this material in the larger cell system, and the same material was then found to be slightly selective for ethanol. The total permeate mass flux obtained in that run was also appreciably higher (2,300 g/m^{2}h compared to 1,400-1,800 g/m^{2}h) even though the film was of the same thickness and in both cases feeds of near 50 percent ethanol were used. There was no obvious explanation for the discrepancy in results.

6.1.3 Neoprene W

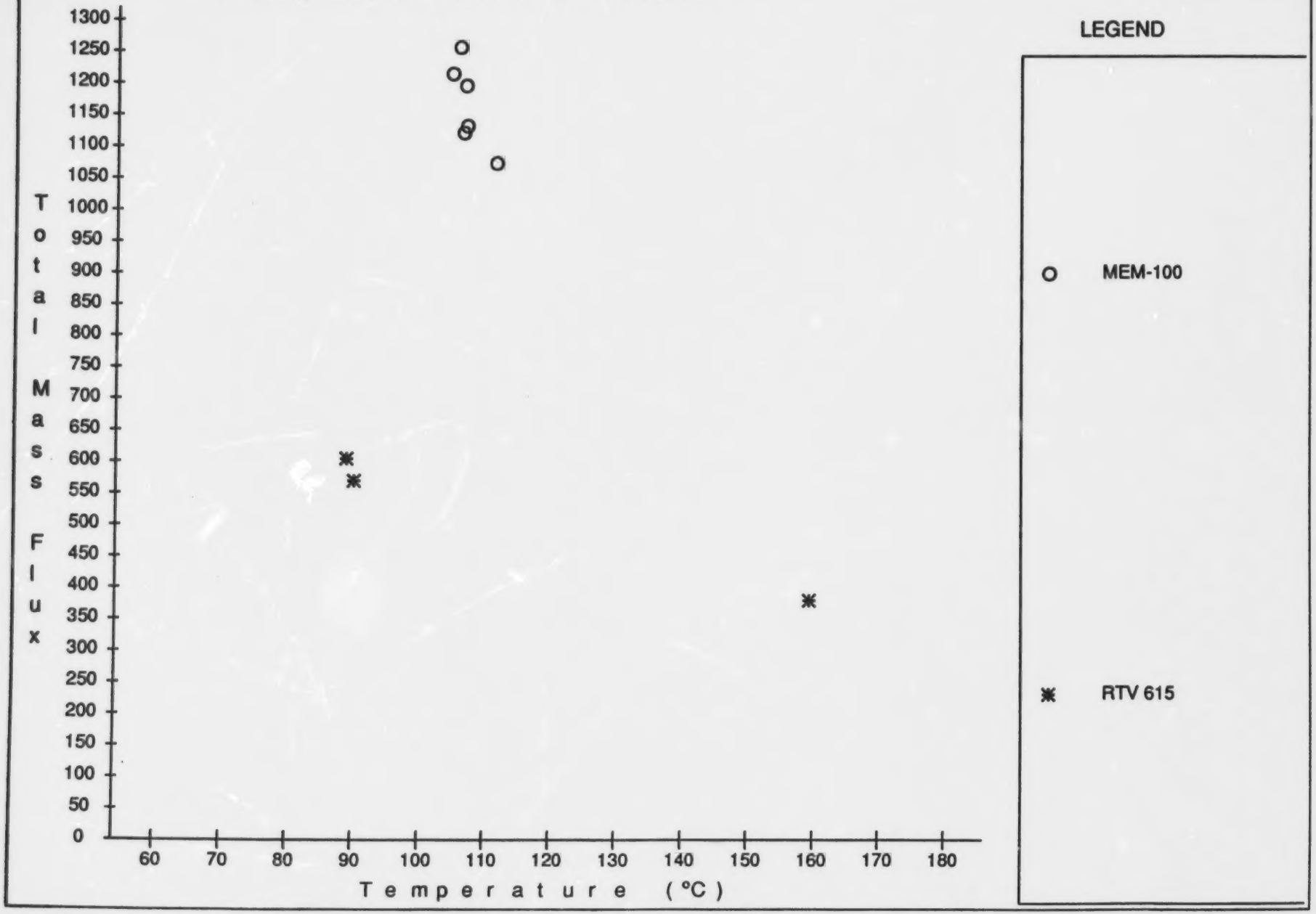
Two different coupons from the same cast sheet of Neoprene W were tested in the small cell system. The sequence of feed and the intermediate room temperature nitrogen permeation test results are listed as follows:

	Feed Sequence	N2 (mL/min)
Coupon No. 1:	Nitrogen Flux	0
	Ethanol	
	Water	
	Nitrogen Flux	51
Coupon No. 2:	Nitrogen Flux	0
	50% Mixture	
	Nitrogen Flux	33
	Water	
	Nitrogen Flux	83
	Ethanol	
	Nitrogen Flux	103

For both coupons, the fluxes of ethanol, water (and 50 percent ethanol in the case of second coupon) were not stable and always declined over time throughout any individual run. The pure ethanol flux was

Figure 17. Total Membrane Mass Flux for Silicone Films

Flux (g/m2h) as a Function of Temperature



relatively higher than water in both cases although there were differences in absolute flux values between coupons. While declining feed flux was found during runs, the nitrogen permeability of the coupons at room temperature between runs was found to substantially increase. This inferred possible pin-holing or other detrimental effects. When observed under the microscope, the used coupons were discoloured and had a pitted surface appearance, but no holes or pores were found. In addition, the Neoprene was observed at points to have essentially extruded through the filter paper backing.

A 50 percent ethanol mixture was used on the second coupon. Due to the small sample size of mixture permeates, analysis was conducted on the GC, with the following results:

Sample	Time (h) from Start	Duration (h)	Sample Size (g)	Flux g/m2h	Composition wt% EtOH
Feed					49.7
No. 1	0.83	0.5	0.77	1,440	11.6
No. 2	2.50	0.5	0.71	1,330	10.5
No. 3	5.50	0.5	0.69	1,290	14.1

Ethanol permeate samples from the second coupon were also analyzed by GC and showed a very slight drop in ethanol concentration indicating water pickup from air leakage into the permeate vacuum side to be negligible.

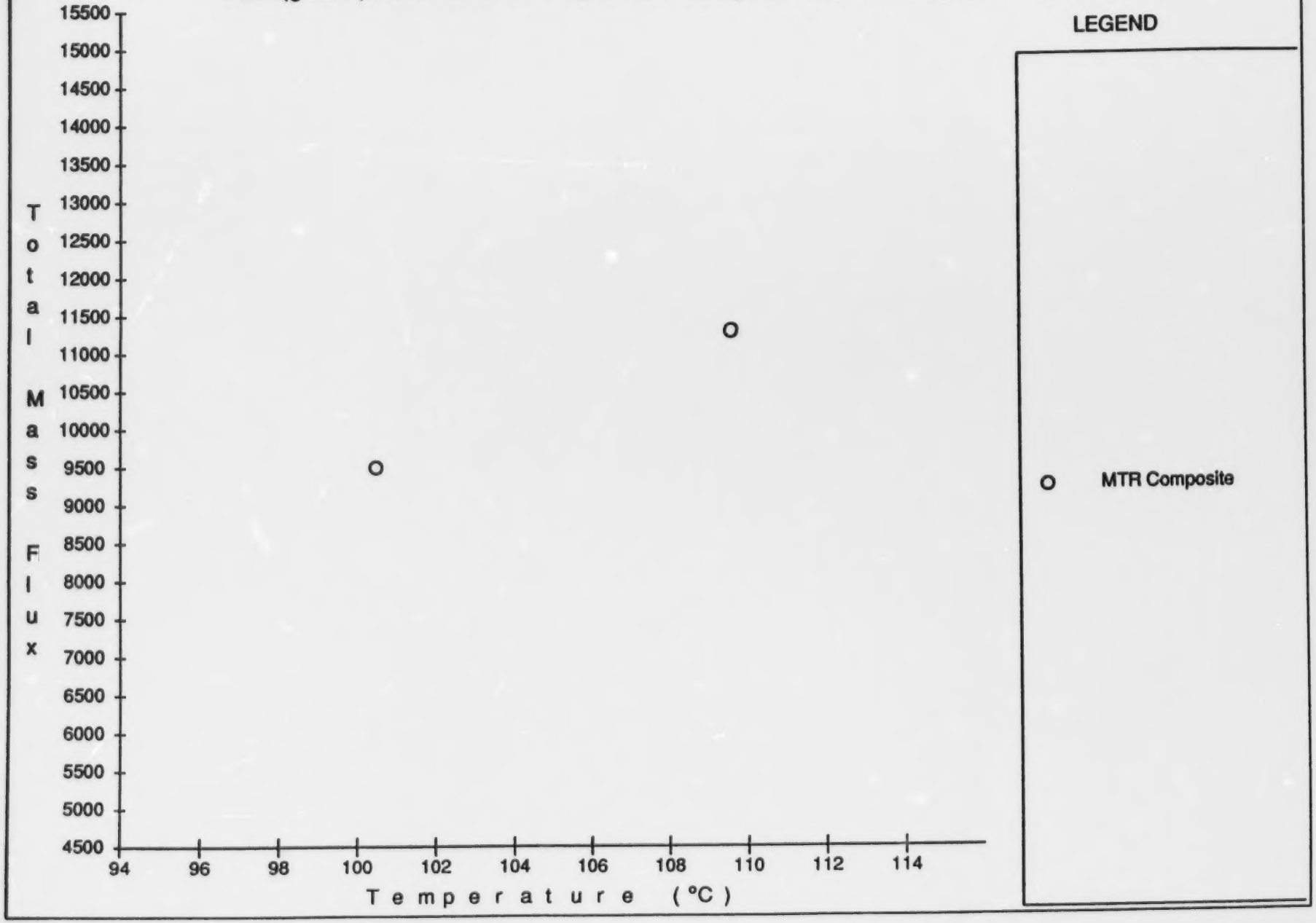
Remaining thin dense film samples of the neoprene not used in tests were found to have discoloured after several months of being left in air in a similar manner to those that were run in the test system Neoprene W was unsuitable at the temperatures considered since it appeared to be degraded by the presence of hot ethanol or water vapours, and because it did not exhibit the proper selectivity.

6.1.4 Fluorel FC-2174

Two different coupons of the fluoroelastomer fluorel from the same cast sheet were tested in the small cell system. The sequence of feed and the intermediate room temperature nitrogen permeation test results are listed as follows:

Figure 18. Total Membrane Mass Flux for MTR Composite Membrane

Flux (g/m2h) for Silicone on Polysulfone Composite as a Function of Temperature



	Feed Sequence	N2 (mL/min)	Permeation (kg/m^2h)
Coupon No. 1:	Nitrogen Flux	300	
	Ethanol		+++
	Nitrogen Flux	+++	
Coupon No. 2:	Nitrogen Flux	24	
	Water		
	2.0 h		31
	4.0 h		33
	Nitrogen Flux	+++	

Fluorel coupons were examined under the microscope prior to being installed in the test system and did not appear to have any visible defects. Even so, the nitrogen permeability of both coupons was noted to be very high prior to use (the highest of any materials tested).

The fluxes through the fluorel coupons were very high, especially for ethanol. The flow of ethanol permeate overloaded the permeate cold trap even for sample times as short as three minutes. The nitrogen permeability of the coupons was extremely high after exposure to either ethanol or water vapour, being too high to measure properly with a 50 mL bubble meter tube.

When removed and observed under the microscope, the coupons were found to contain visible pore holes. The coupon exposed to ethanol had numerous holes of roughly 50 µm diameter. The water vapour exposed coupon also had pores but far fewer in number (i.e. four to five over coupon area). Mixtures were not tested with a Fluorel coupon in the small cell. However, the results showing large hole formation corroborated an earlier test run using a 50 percent ethanol feed mixture in the large cell where very large flux and virtually no separation were found.

Thus while fluorel was resistant to high temperatures, it tended to be too porous and readily developed holes after exposure to ethanol or water vapour, making it unsuitable.

6.1.5 Nitrile Rubber (Butadiene-Acrylonitrile (19.65 percent)

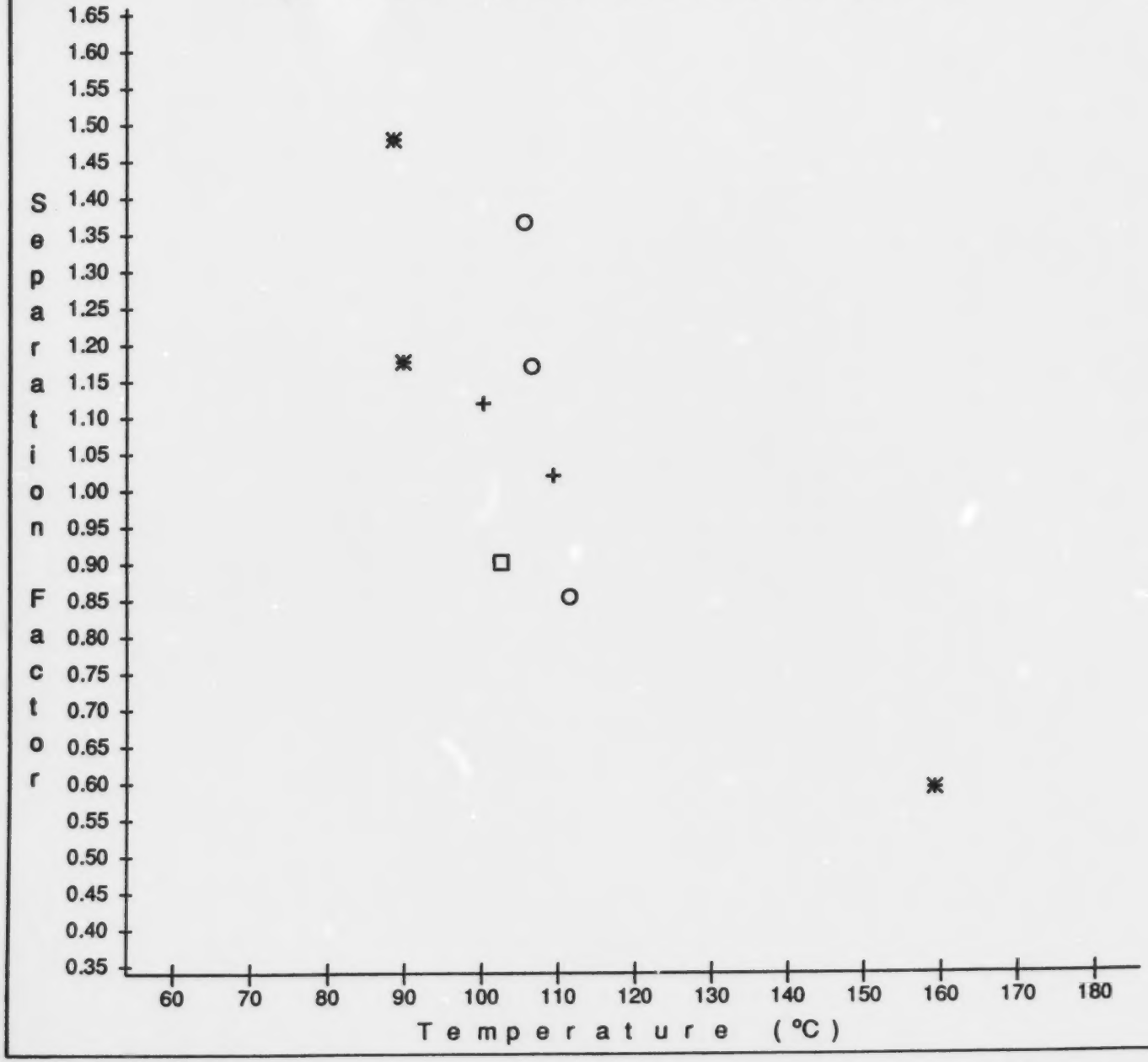
The nitrile rubber coupon showed negligible initial nitrogen permeation, but was found to be excessively permeable when actual feed was applied at elevated temperature (i.e. permeate collection tubes were overloaded after very short sample times).

6.1.6 Hypalon 20

A hypalon coupon was put into the cell but found to have a very high nitrogen permeation flux; too high to be further tested.

Figure 19. Selectivity Comparison of all Silicone Films Tested

Separation Factor [αew] as a Function of Temperature



LEGEND

- MEM-100
- RTV 615
- MTR Composite
- Silgard 184

6.2 Other Non-Polysulfone Polymers

6.2.1 Polyimide

Runs were conducted in the small cell system using both pure water and pure ethanol on two films of different thicknesses (40 and 15 μm). Permeation of nitrogen at room temperature was not detectable before or after any runs. Although the polymer was physically unaffected by the presence of vapours, the selectivity was not determined. Permeation fluxes for pure water and absolute ethanol were extremely low, even when using a film of only roughly 15 μm thickness, and runs were not conducted using ethanol/water feed mixtures. Nakamura and Makino (1987), however, employed asymmetric polyimide membranes for vapour phase separation of ethanol and water, and reported selectivity to water.

6.2.2 Parylene "C"

A single run was conducted using a 1 mil (25 μm) Parylene C coupon in the small cell system with a feed mixture near 50 percent ethanol. As in the case of polyimide, there was no detectable nitrogen permeation either before or after the run indicating that the film did not suffer adverse effects. The flux obtained was extremely low and it was possible to draw the small amount of permeate into a GC syringe for analysis.

Despite the fact that this polymer is recognized in the literature to have extremely low water permeability, the permeate nevertheless appeared to have been enhanced in its concentration of water. The concentration of ethanol in the permeate was less than one percent and was much lower than in the feed.

6.3 Polysulfones

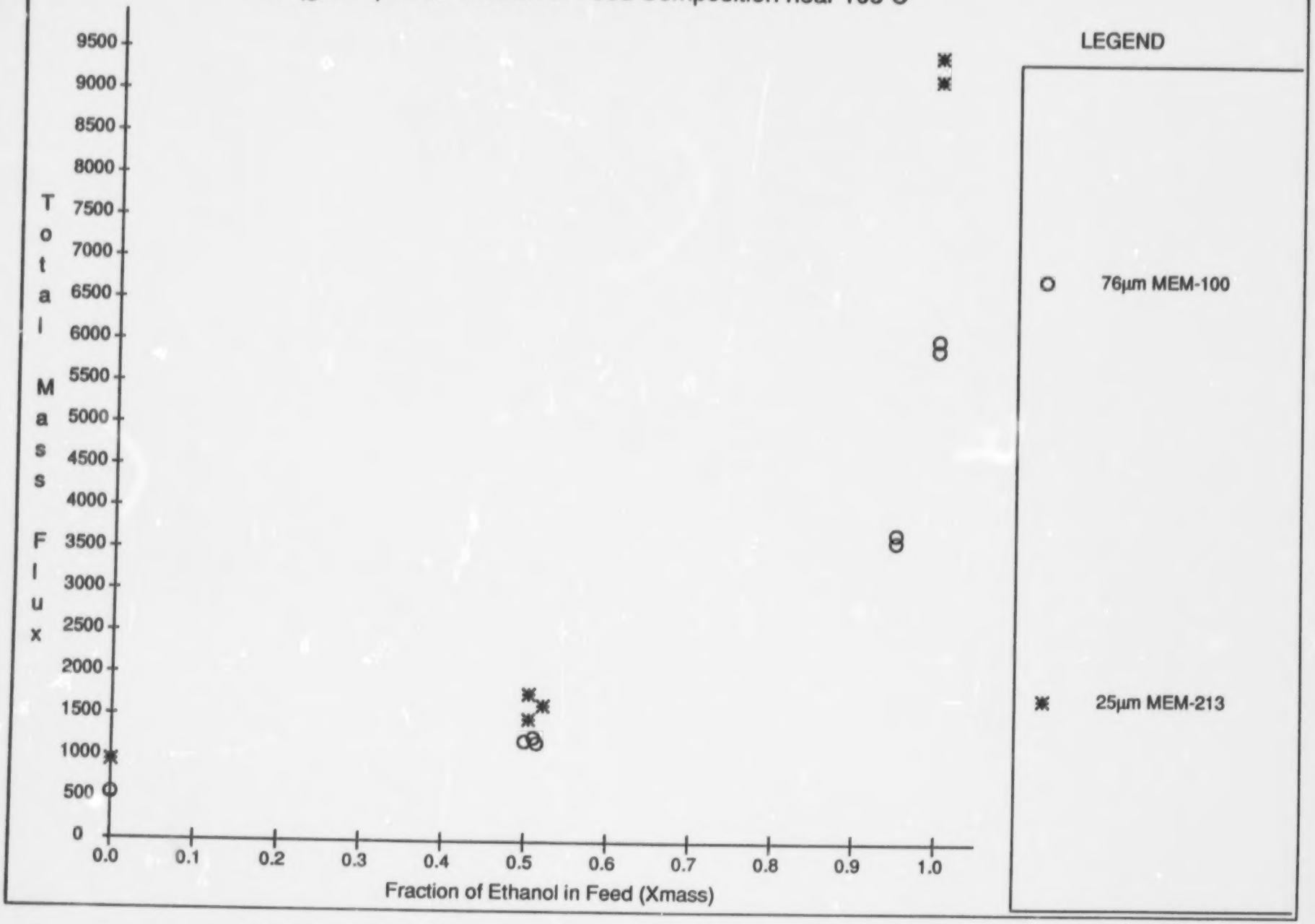
6.3.1 Udel P3500 Polysulfone

Runs were conducted using thin 50 μm dense films of Udel cast from chloroform solution in the small cell. The permeation flux of pure water vapour was found to be very low, much lower than silicone, with the ratio of pure water permeability coefficients of Udel to Silicone at 105°C only 0.15.

Udel films, however, could not tolerate pure ethanol vapour, and lasted less than about 4 h in the small cell before completely shattering. A "shattered" polysulfone film exposed to ethanol vapour in the small cell is pictured in Plate 1.

While no work was done using mixtures in the small cell, three different Udel films and membranes were tried in the large cell using feed mixtures near 50 percent. Two thin dense films, one cast from

Figure 20. Total Membrane Mass Flux for MEM-213 Silicone-Polycarbonate Flux (g/m2h) as a Function of Feed Composition near 105°C



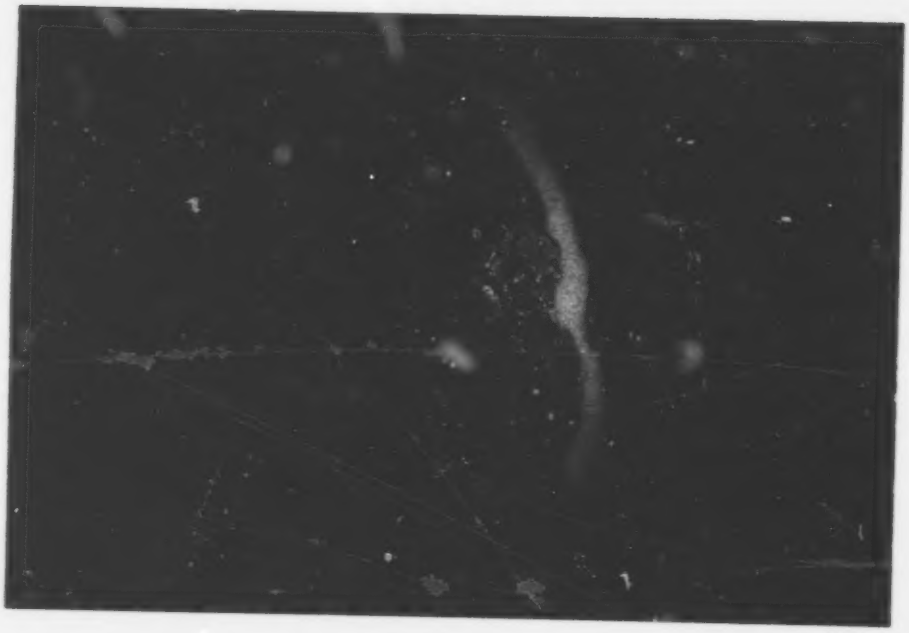


Plate 1. Udel Polysulfone Dense Film from Chloroform Solution. Film Exposed to Vapour Ethanol in the Small Membrane.

dichloromethane solution into an alcohol bath, and the other cast from an NMP solution and evaporated, were both found to have shattered like the film in the small cell. Both these films were initially clear, but underwent a change in transparency after exposure to ethanol. The film of Udel cast from an NMP solution changed from clear to opaque white, similar to the observed colour changes when asymmetric membrane are formed through the gellation/solvent exchange process by being immersed in water. An asymmetric Udel ultrafiltration membrane was also tested in the large cell system using a feed mixture near 50 percent, and the membrane was also destroyed, although not in the same dramatic fashion.

In an attempt to quantify the destructive effect of ethanol on Udel polysulfone films, strips of thin dense Udel film from NMP solutions were tested in an Instron Unit for tensile strength after being dipped into boiling 95 percent (azeotropic) ethanol for specific periods of time. As illustrated in Figure 22, the tensile strength at break decreased with increasing exposure to boiling ethanol. The coupons also became progressively more opaque, with the 10 minute coupon being completely white. As well as becoming weaker, the coupons also appeared to have become more plastic, showing increasing elongation before breakage.

6.3.2 Victrex Polysulfone

One thin dense film Victrex coupon of 70 µm thickness was run in the small cell using 95 percent (azeotropic) ethanol feed. Nitrogen permeation and flux results are listed as follows:

Feed Sequence	N2 (mL/min)	Permeation (g/m^2h)	Temp (°C)
Nitrogen Flux	0		
Ethanol for 5 h			
1.5 h		75	84.5
4.0 h		56	90.9
Nitrogen Flux	160		

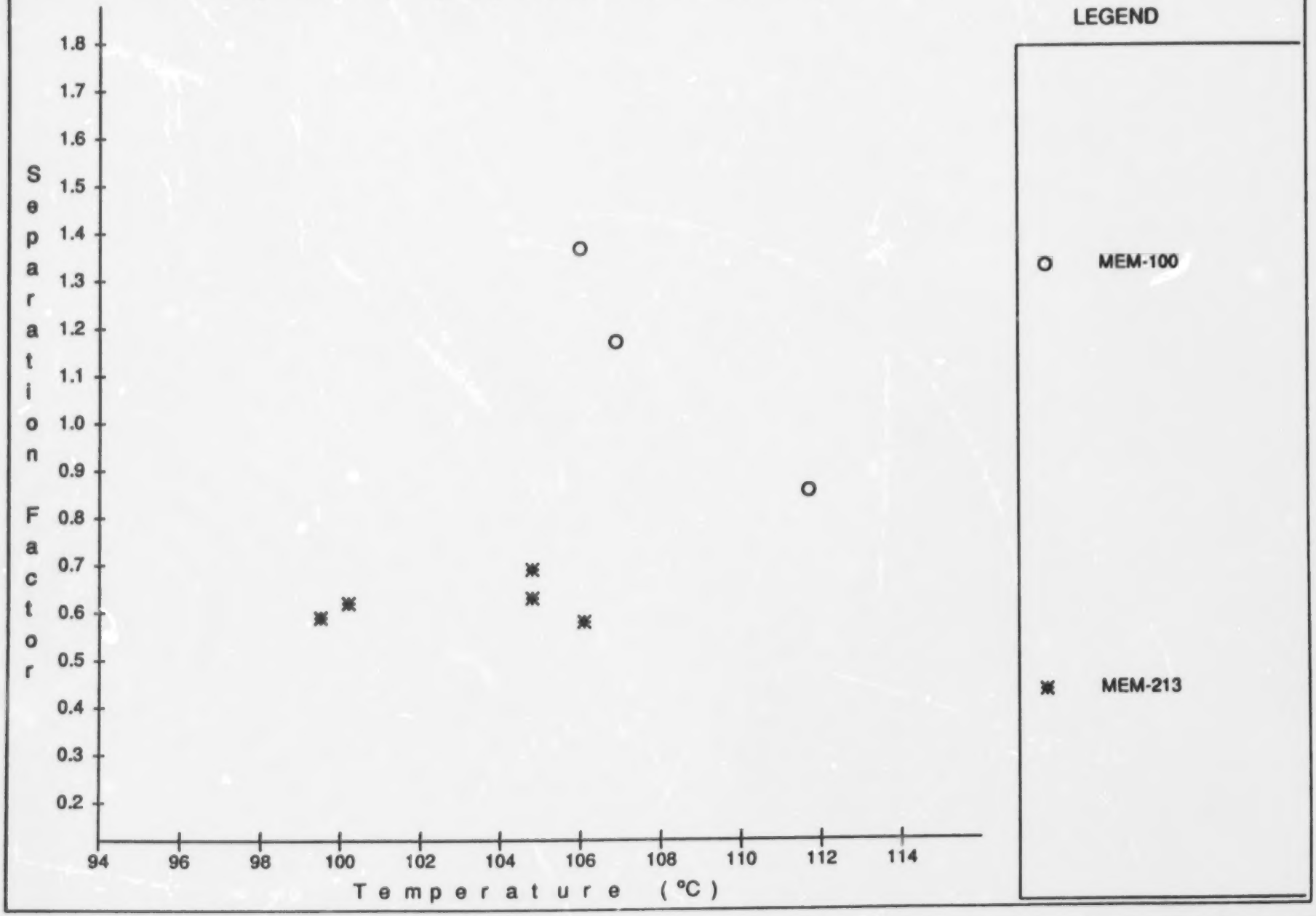
The flux through the membrane was quite small, and no analyses were performed to determine the composition of permeate. Flux appeared to decline with exposure time, however, this may have also been influenced by the operating temperature which was also changed during the run. Initially, there was no visible nitrogen permeation at room temperature. After the run, however, the nitrogen flux was very high, being 2.6 mL/s, although there was no visible damage to the coupon.

6.4 Modified Polysulfones

6.4.1 Di(Trimethylsilyl) Udel Polysulfone

A coupon of thin dense film cast from a chloroform solution was tested in the small cell using approximately 50 percent ethanol feed. Prior to being run with feed, there was no visible permeation of nitrogen by the

Figure 21. Selectivity of MEM-213 Silicone-Polycarbonate to Ethanol
Separation Factor [αew] as a Function of Temperature



coupon. The coupon, like ordinary polysulfone, did not tolerate the presence of ethanol vapour and "shattered" after less than one hour exposure to feed. Even without exposure to ethanol vapour, this material was found to very brittle with poor mechanical strength, such that pieces of the film sheet could be pulled apart easily by hand.

Earlier, a coupon of each of the membranes cast from DMA solution into ethanol and water was tested for pure liquid water permeability in a standard ultrafiltration test system. Water-cast membranes permeated liquid water while ethanol-cast membranes did not. Accordingly, alcohol-cast membranes were employed in the large cell system using 50 percent ethanol feed. There was no selectivity exhibited. The permeate flux through the membranes were very large such that it was difficult to maintain either pressure in the cell or a continuous flow of non-permeate return to the feed reservoir. The membranes were found to be damaged by exposure, being cracked and split.

6.4.2 Di(Butyl) Udel Polysulfone

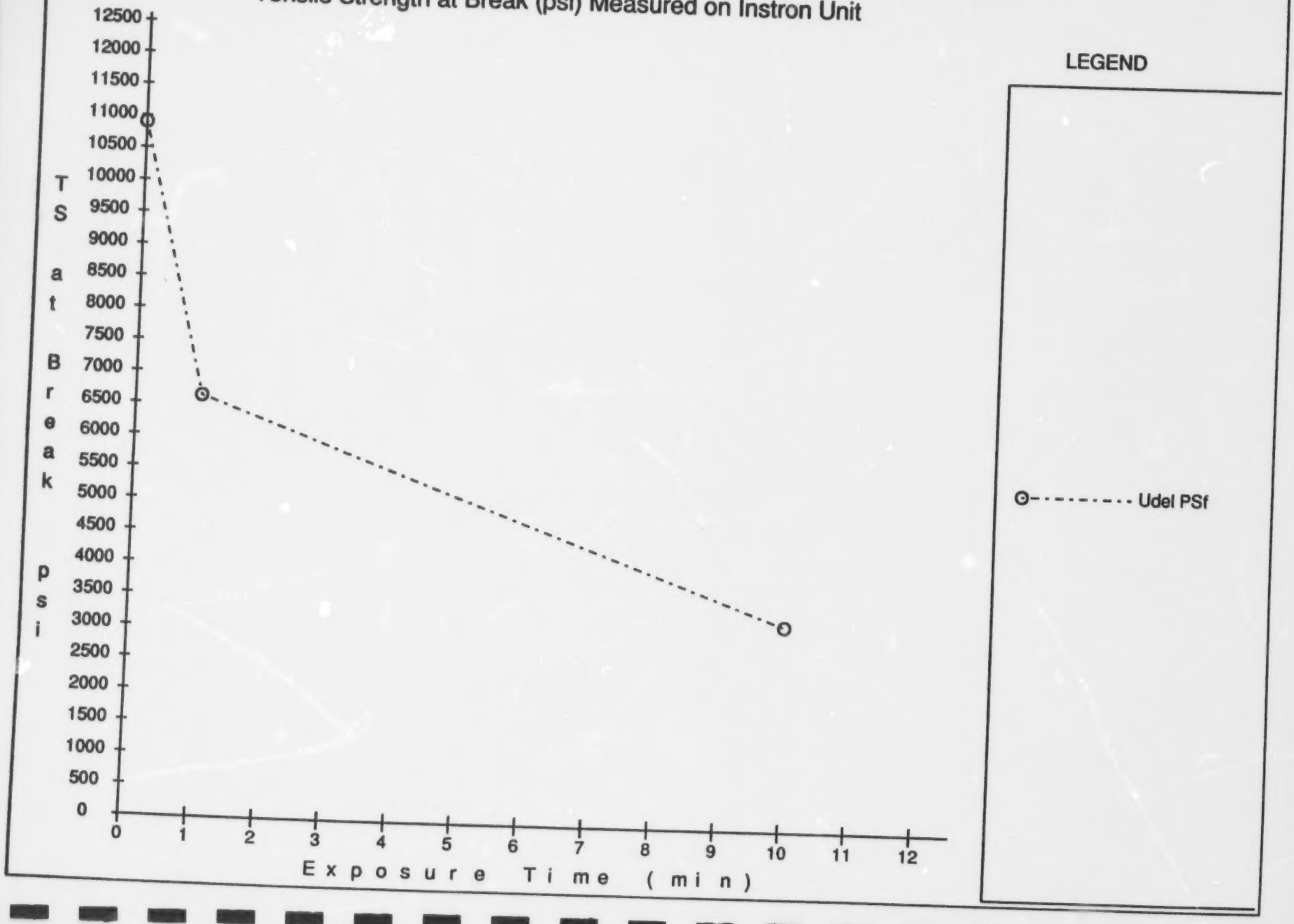
A coupon of thin dense film 50 μm in thickness that was cast from a chloroform solution was tested in the small cell using absolute ethanol as feed. The results of room temperature nitrogen permeation tests as well as permeate fluxes are listed in sequence as follows:

Feed Sequence	N2 (mL/min)	Permeation (kg/m^2h)
Nitrogen Flux	0	
Ethanol for 2.75 h		
1.0 h		25.3
2.0 h		30.5
2.5 h		44.5
Nitrogen Flux	1200+	

Although only exposed to the feed ethanol vapour for a short period of time, the flux through the membrane was high and increased with time. The permeation of nitrogen through the membrane at room temperature was also found to increase drastically as a result of the ethanol exposure. When removed from the cell the coupon was observed to have not experienced a catastrophic failure as was the case with Udel polysulfone. While the membrane appeared more or less intact, the central portion exposed to the ethanol vapour was adhered to the filter-paper backer, also with some evidence of extrusion through the backing as was observed in the case of neoprene. This was likely due to plasticization of the polymer. The T_g, or glass transition temperature, of di(butyl) Udel polysulfone under defined conditions is approximately 115°C. Because of the presence of the hot ethanol vapour, the transition to rubbery state appeared to have occurred at the lower temperature under which the run was conducted (i.e. 102-103°C).

In an attempt to test possible protection of the polysulfone from direct vapour attack, a di(butyl) coupon was laminated with RTV 615 silicone. This film of roughly 175 μm thickness (50 μm polysulfone plus 125 μm silicone) was run using absolute ethanol as feed. The

Figure 22. Tensile Strength of Udel Polysulfone Exposed to Boiling Ethanol



nitrogen permeation and permeate flux results are as follows:

Feed Sequence	N2 (mL/min)	Permeation (g/m^2h)
Nitrogen Flux	0	
Ethanol for 4.5 h		
1.0 h		93
2.0 h		3100
Nitrogen Flux	309	

The ethanol flux through the coupon increased from a very low early value to a high value further on in the run. The room temperature nitrogen permeation also went up significantly after exposure to the ethanol vapour from a negligible initial value to a value which was lower than that found for di(but-1) alone, but much higher than of silicone alone. When the coupon was removed, the laminated silicone layer had separated, with the di(butyl) in the central portion of the coupon adhered to the filter-paper backing. The lamination appeared to have had little positive effect.

In an earlier attempt using asymmetric type membranes, pure liquid water permeability tests were done in a standard ultrafiltration test system on the di(butyl) membranes from DMA solution cast both into water and ethanol. As in the case of the di(trimethylsilyl) polysulfone, the water-cast membranes permeated water while ethanol-cast membranes did not. Alcohol-cast membranes were employed in a test run in the large cell system using 50% ethanol feed, but showed no selectivity. The permeate flux through the membranes was very large such that it was difficult to maintain pressure in the cell or a continuous flow of non-permeate return to the feed reservoir. The di(Butyl) membranes developed visible pinholes but were intact even though they were subjected to expansion.

6.4.3 Di(Hydroxy) Udel Polysulfone

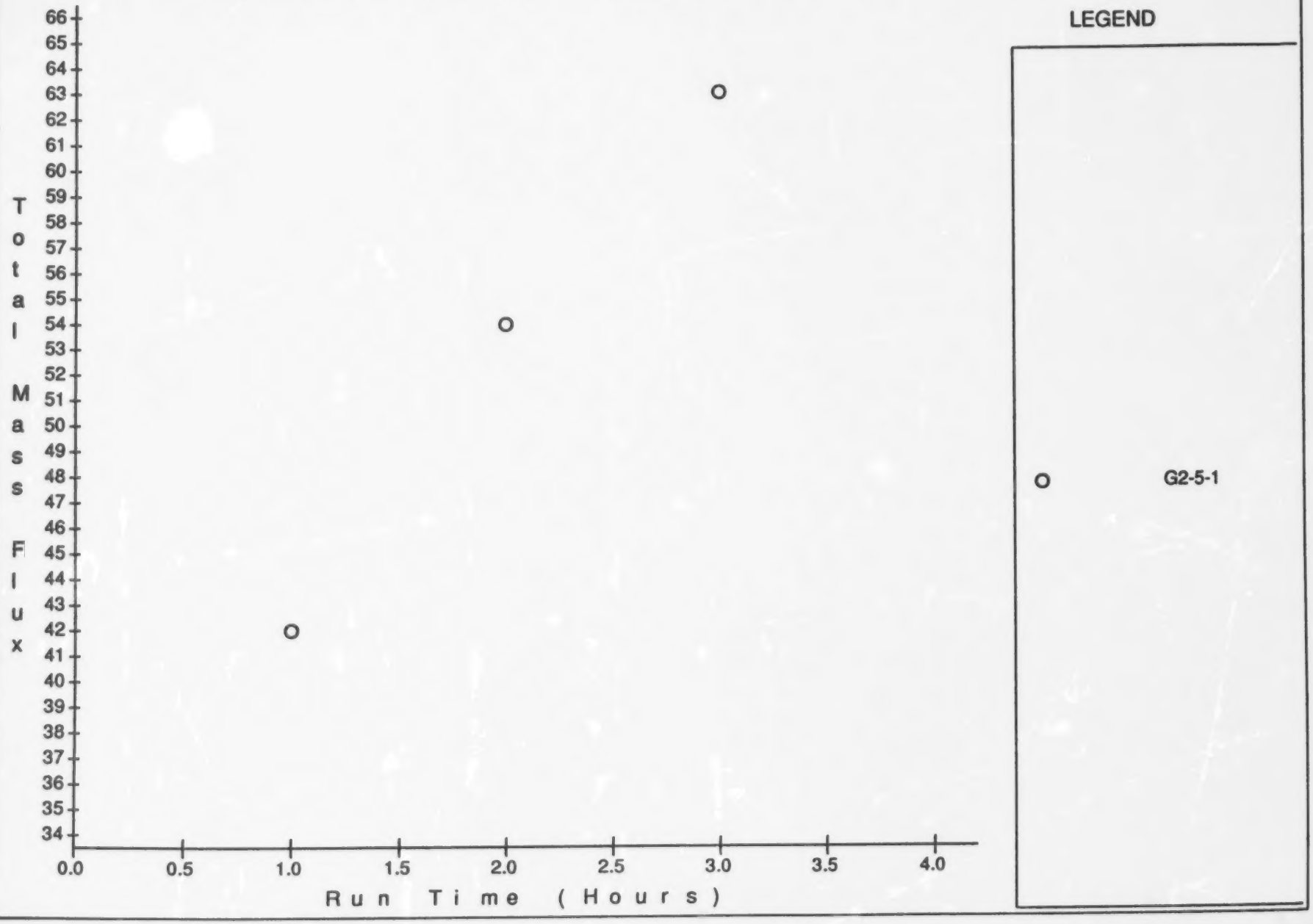
A coupon of thin dense film 50 μm in thickness that was cast from a chloroform solution was tested in the small cell using absolute ethanol as feed. The results of room temperature nitrogen permeation tests as well as permeate fluxes are listed in sequence as follows:

Feed Sequence	N2 (mL/min)	Permeation (kg/m^2h)
Nitrogen Flux	0	
Ethanol for 3.5 h		
0.75 h		17.3
3.25 h		16.3
Nitrogen Flux	460	

The sample coupon was exposed to ethanol vapour for 3.5 h. The ethanol flux measured during this time was high, although much lower than the di(butyl) case, and declined slightly with time. The room temperature nitrogen permeation also increased after exposure but again not nearly as high as with the di(butyl). When removed from the cell, the coupon

Figure 23. Permeate Mass Flux for G2-5-1 Carboxylated Polysulfone Coupon

Increase of Flux (kg/m2h) with Exposure Time



was found to be intact and was not adhered to the filter-paper backer except for a few points. Although intact, the central portion exposed to the ethanol vapour was very mottled in appearance, almost opaque.

6.4.4 Carboxylated Udel Polysulfone

Test runs were performed in the small cell system on carboxyl modified Udel polysulfones which contained 0.25, 0.40, 0.60 and 0.63 equivalent carboxyl substitutions per polymer repeat unit.

Test runs were preformed initially on two 0.25 equivalent substituted membrane coupons (MG300-B4-4 and MG300-B4-2) cast from DMA into water by M. Guiver of NRC. Runs were conducted using both 50 percent and 95 percent ethanol feeds with the following results:

Coupon	Nitrogen (mL/min)	Temp (°C)	Flux (g/m^2h)	Feed	Perm	α_{ew}
B4-4	0	89	140	0.95	0.26	0.018
B4-2	0	82	112	0.95	0.30	0.025
	0	94	196	0.51	0.12	0.130

Both 0.25 substituted coupons showed no apparent deterioration as a result of exposure, with room temperature nitrogen permeation rates not increasing after being run with 95 percent ethanol feed. The second coupon was observed to break, with very high nitrogen flux observed, however, failure did not actually occur during the run as there was no observed loss of vacuum. Even then, the film did not fail in a catastrophic manner as had normal Udel, but instead there were only a few surface breakage points. The coupons were slightly opaque prior to being tested in the cell, but were both observed to have gone clear as a result of exposure.

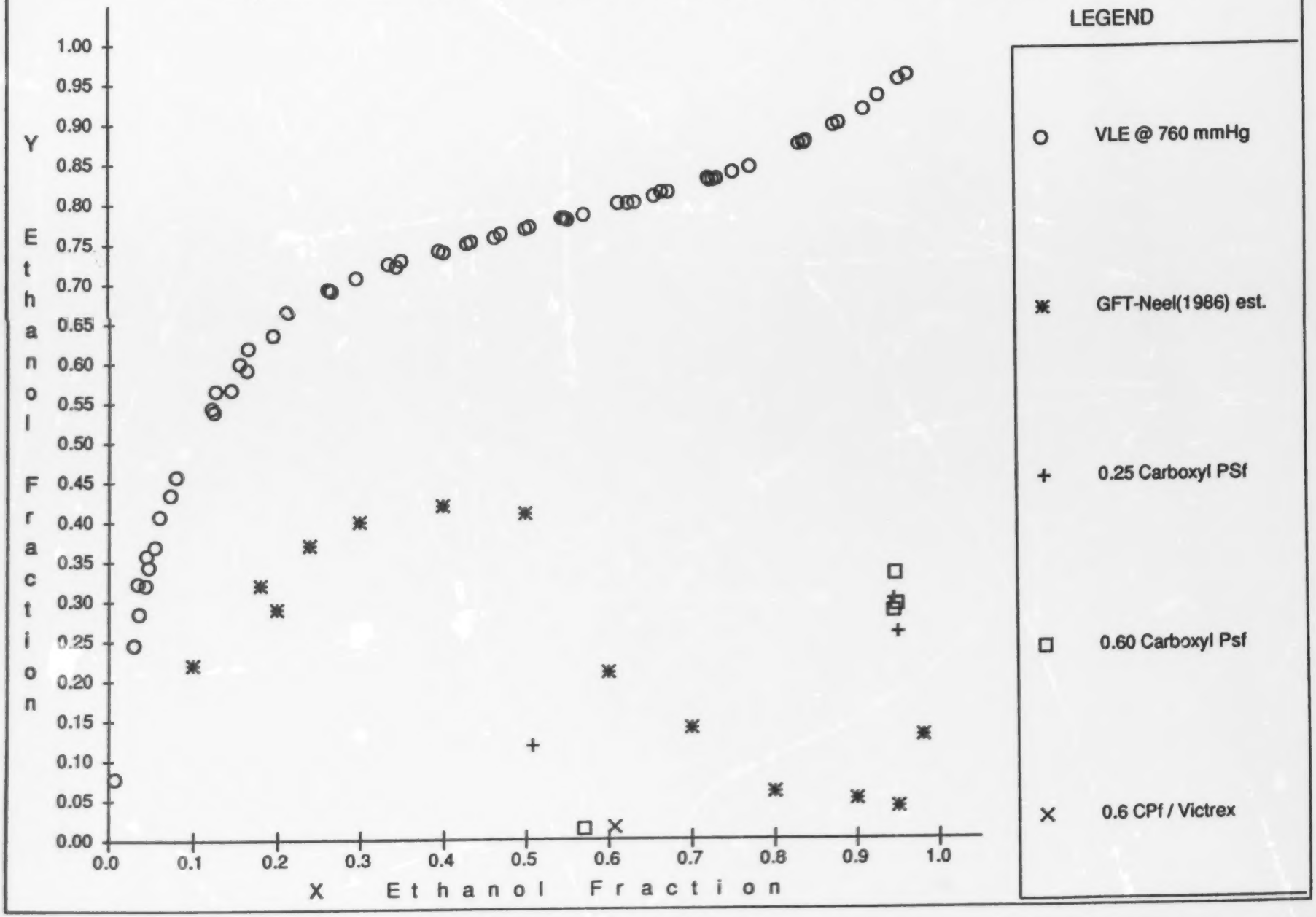
Both of these coupons exhibited remarkably high selectivity toward water. In both cases the permeate ethanol concentrations were on the order of 26-30 percent (i.e. water concentration going from 5 percent in the feed to 70-74 percent in the permeate). The feed, which was recycled, became slightly but progressively enriched in ethanol over time. On the basis of these encouraging observations other carboxylated membranes were tested.

A coupon of 0.40 equivalent polymer cast from an NMP solution (OKNMP 84-4), also supplied by M. Guiver was tested using 95 percent ethanol feed, but was shattered after exposure to the vapour ethanol, like ordinary Udel. This membrane was more open to begin with, having an initial nitrogen permeation of 1.05 mL/min.

Two other porous carboxylated polysulfone membrane coupons made of 0.63 equivalent polymer cast from DMA solution (G2-5-4 and G2-5-1) obtained from M. Guiver were run using approximately 50 percent ethanol feed. These membranes were much more open with initial nitrogen fluxes of 150 mL/min and 1,000 mL/min respectively. The permeate flux in both cases was very high. In the case of the G2-5-4 coupon, which was boiled

Figure 24. Selectivity Results for Carboxylated Polysulfone Coupons

Separation Factor [αew] Compared to V-L Equilibrium and GFT Pervaporation Membrane



in water, the permeate collection tubes were overloaded. The membrane did, however, appear to exert some selectivity toward water, with the concentration of ethanol in two accumulated permeate samples being reduced to 39 percent and 43 percent.

The second coupon, G2-5-1, which was solvent exchanged from water to ethanol, on the other hand showed little change in ethanol concentration, being if anything marginally higher in the permeate. The lack of selectivity with the G2-5-1 as compared to the earlier coupon can not be conclusively explained. The latter coupon was much more open at the start of testing, which may have been indicative of its lack of selectivity. To what extent the lack of selectivity may have resulted from the difference in post-treatment method employed is not certain. The permeate flux in the case of the G2-5-1 coupon was also found to increase progressively with time as indicated in Figure 23. For both these membranes, damage was noted on the membrane surface, appearing as "cuts" or "nicks". Damage, however, tended to be localized and the coupons were still intact after testing.

Runs were lastly conducted on four films made from 0.60 equivalent polymer cast from DMA solutions (A1-1, B1-1, A1-3 and A1-5). In all four cases, there were negligible initial nitrogen permeation, suggesting that the skin layers for all were quite thick relative to the total membrane thickness.

The A1-1 (Carb PSf only) and B1-1(0.5 of Carb PSf/0.5 of Victrex) coupons were run using 50 percent ethanol feed. In both cases, the fluxes were very low, but the selectivities very high as noted in the sequence as follows:

Coupon	Nitrogen (mL/min)	Temp (°C)	Flux (g/m^2h)	Feed	Perm	α_{ew}
A1-1	0	97	103	0.57	0.013	0.0099
B1-1	0	96	121	0.61	0.015	0.0099

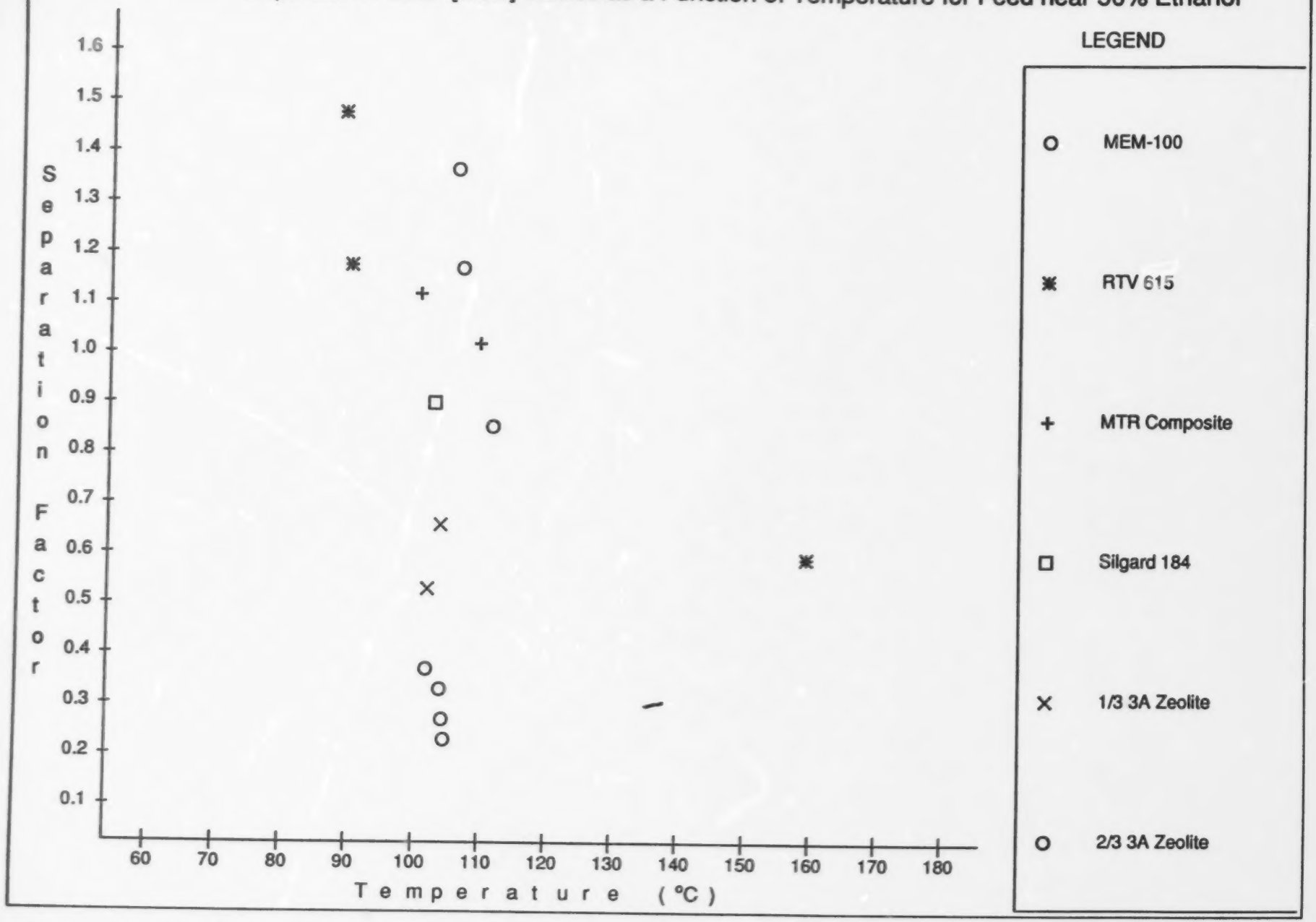
In both cases the permeate ethanol concentration was less than 2 percent. The selectivity with respect to water, α_{we} which is equal to $1/\alpha_{ew}$, was over 100 in both cases which represented the best selectivity of any kind obtained in the entire project.

Both membranes were damaged by the exposure to feed, but again failure did not actually occur during the run itself and damage was very localized. It was specifically noted in one case that membrane failure occurred after the run was completed (i.e. sudden loss of vacuum during shutdown).

Two more coupons (A1-3 and A1-5) were run using 95 percent ethanol feed with one coupon run for 16 hours. The fluxes and selectivities achieved are listed as follows:

Figure 25. Selectivity of Silicone Films Incorporating 3A Zeolite

Separation Factor [αew] Values as a Function of Temperature for Feed near 50% Ethanol



Coupon	Nitrogen (mL/min)	Temp (°C)	Flux (g/m^2h)	Feed	Perm	α_{ew}
A1-3	0	93	206	0.95	0.29	0.023
A1-5	0					
1.0 h		91	168	0.95	0.33	0.028
14.0 h		91	159	0.95	0.29	0.022

Breakage of the coupon was noted in one of these cases, but again this failure was observed during shutdown and not while actually exposed to feed. The fluxes were very small and good water selectivity was achieved with permeate ethanol concentrations in the range of 29 percent to 33 percent.

The separation results of the dense film 0.25 and 0.60 equivalent carboxylated polysulfones are summarized in an X versus Y composition diagram in Figure 24. The results are compared with vapour-liquid equilibrium at 760 mmHg, and with selectivity data for a commercial GFT composite pervaporation membrane estimated from Neel (1986). When using 95 percent (azeotropic) ethanol as feed, the permeate concentrations achieved by films at the two degrees of carboxylation were fairly similar, although higher in ethanol content than what could be achieved by a GFT dehydration membrane. With feed concentrations closer to 50 percent, the permeate ethanol concentration was clearly much lower in the case of the 0.6 equivalent films than the 0.25 equivalent. Both were also much lower than the permeate ethanol concentration from a GFT membrane at this point, and lower in the case of the 0.6 equivalent film than what could be achieved by pervaporation using dense films of either polyacrylonitrile or polyvinylalcohol as also presented in Neel (1986). These results showed the carboxylated polysulfones to have very good water selectivity relative to commercially available materials, and also indicated that at certain feed concentrations, the selectivity of the film for water was dependent on the degree of carboxylation of the polymer.

6.5 Selective Additives in Silicone

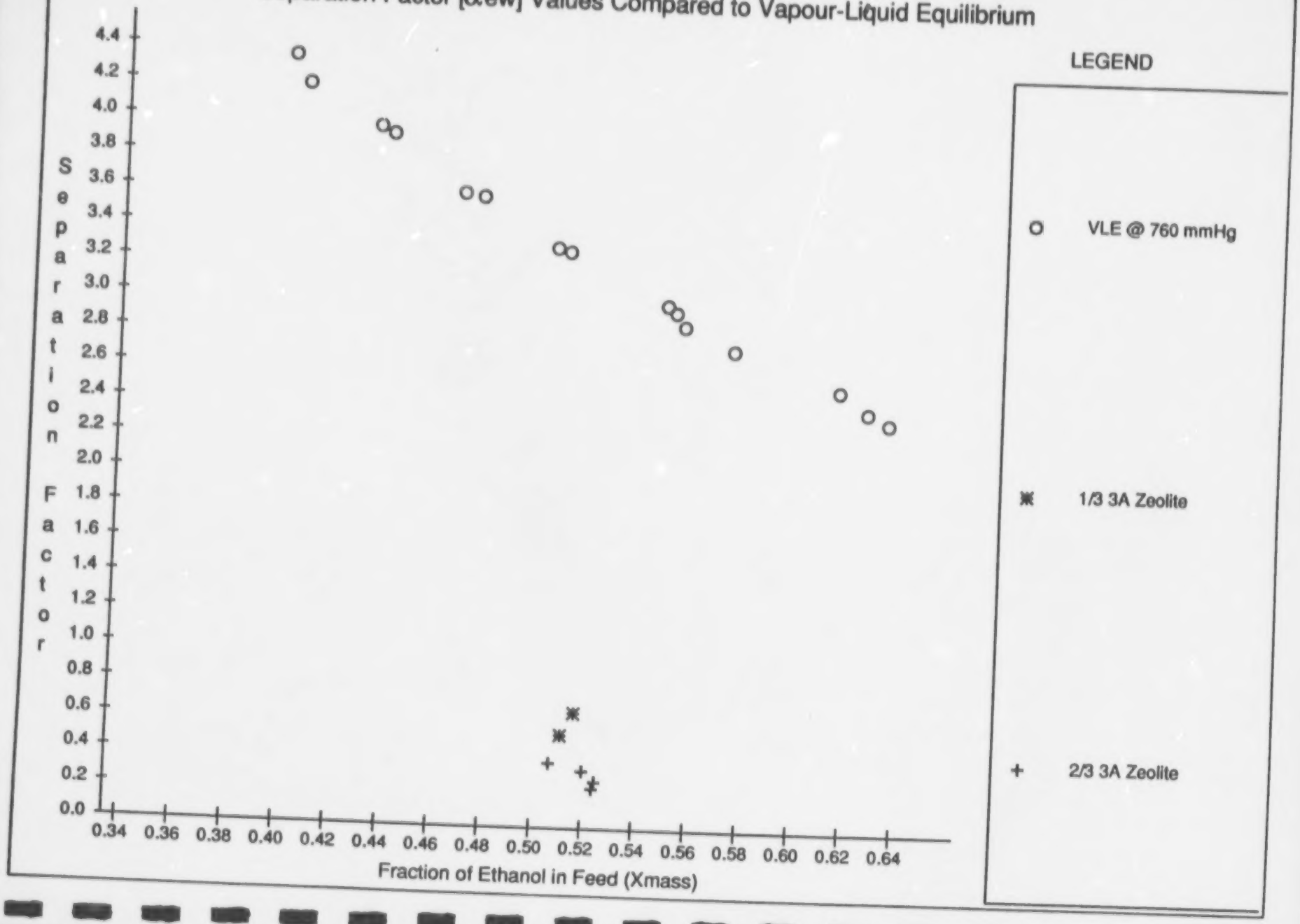
6.5.1 Zeolites

General:

For all of the zeolite/silicone films tested, both hydrophilic 3A and organophilic S-115, the room temperature nitrogen permeation was quite high. Using a published nitrogen permeability coefficient for silicone, effective thicknesses were estimated based on initial fluxes. Estimated thicknesses were always lower than measured thicknesses, and in the case of the 2/3 zeolite- 1/3 silicone films, tended to reflect the approximate thickness of the silicone sealing layer.

Figure 26. Selectivity of Silicone Films Incorporating 3A Zeolite

Separation Factor [αew] Values Compared to Vapour-Liquid Equilibrium



3A Zeolite - Hydrophilic:

Runs were conducted with three different films incorporating 3A zeolite using feed near 50 percent ethanol as follows:

1. 1/3 3A, 2/3 RTV 615, freon diluent, no bottom skin, coupon No.1
2. 2/3 3A, 1/3 RTV 615, freon diluent, bottom skin, coupon No.2
3. 2/3 3A, 1/3 RTV 615, hexane diluent, bottom skin, coupon No.3

The nitrogen permeations observed for these films and their estimated effective thicknesses based on initial fluxes are listed as follows:

Coupon	Measured Thickness (μm)	Initial N2 Flux (mL/min)	Final N2 Flux (mL/min)	Estimated Thickness (μm)
1/3 Freon	120	0.72	0.73	115
2/3 Freon	260	5.30	2.90	16
2/3 Hexane	145	4.10	1.00	20

The 3A zeolite material was expected to enhance water adsorption and thus make the film more water selective. This result was actually observed, with films exhibiting pronounced water selectivity, as well as fairly high permeate fluxes as follows:

Coupon	Run Sample	Temp (°C)	Flux (g/m^2h)	α_{ew} (-)
1/3-Freon	1	102	820	0.53
	2	104	870	0.66
2/3-Freon	1	102	3270	0.37
	2	105	2820	0.23
2/3-Hexane	1	104	1700	0.33
	2	104	1340	0.27

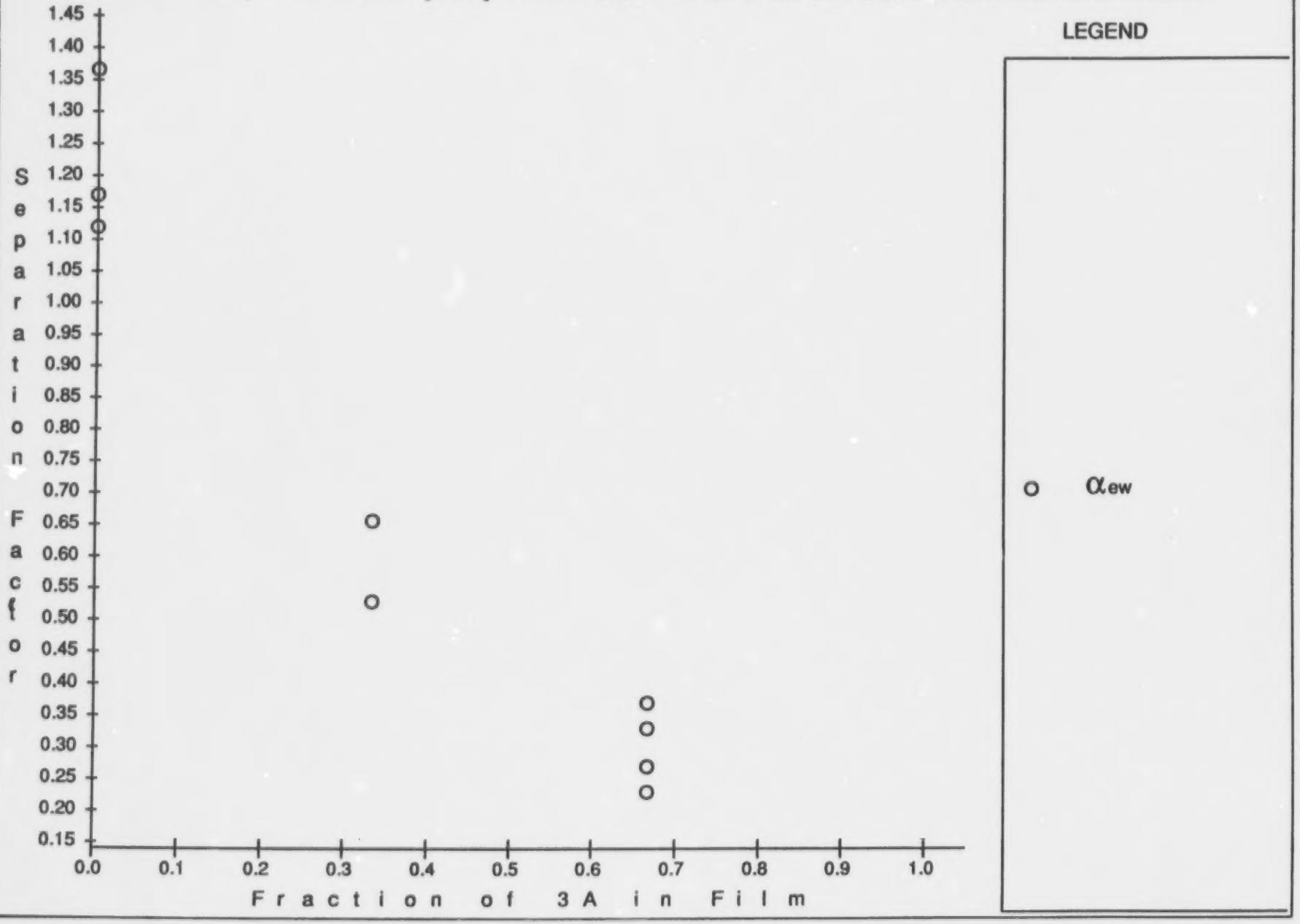
The α_{ew} separation factor results show significant water selectivity as compared in Figure 25 with the other silicones alone, and in Figure 26 with relative volatility values from vapour-liquid equilibrium determined at 760 mmHg constant pressure. As illustrated in Figure 27, the value of the separation factor with respect to ethanol, α_{ew}, decreased as the concentration of 3A in the film was increased. (Note that silicone alone was used for the zero zeolite value.) It was also observed in these runs that non-permeate ethanol concentrations tended to be higher than feed values, and further that the concentration of ethanol in the feed tank tended to increase progressively, indicating a significant dewatering effect.

Based on these results, two films incorporating 3A zeolite were run using 95 percent ethanol as feed in order to test dewatering capability with azeotropic mixtures. The two coupons are described as follows:

1. 2/3 3A, 1/3 RTV 615, freon diluent, bottom skin, coupon No.3

Figure 27. Effect of 3A Zeolite Addition on Selectivity

Separation Factor [αew] Values as a Function of 3A Content for Feed near 50% Ethanol



2. Thick layer (560-580 μm) 3A zeolite/silicone with bottom skin

The nitrogen permeations observed for these films and their estimated effective thicknesses, based on initial fluxes, are listed as follows:

Coupon	Measured Thickness (μm)	Initial N2 Flux (mL/min)	Final N2 Flux (mL/min)	Estimated Thickness (μm)
2/3 Freon	230	5.60	3.50	15
Thick 3A	560	0.32	0.20	260

The flux and separation results are listed as follows:

Coupon	Run Sample	Temp (°C)	Flux (g/m^2h)	α_{ew} (-)
2/3 Freon	1 (1h)	106	9510	
	2 (5h)	100	7720	
	3 (9h)	96	6370	
Thick 3A	1 (1h)	86	600	0.53
	2 (4h)	81	390	0.53

Fluxes were observed in both cases to decline with time, however, these observations also corresponded with decreasing cell temperature so that it is difficult to make a conclusive judgment in this respect. Permeate compositions were not determined in the case of the first film, but were in the case of the thick 3A film with some decrease of ethanol concentration observed from 95 percent in the feed to approximately 91 percent in the permeate.

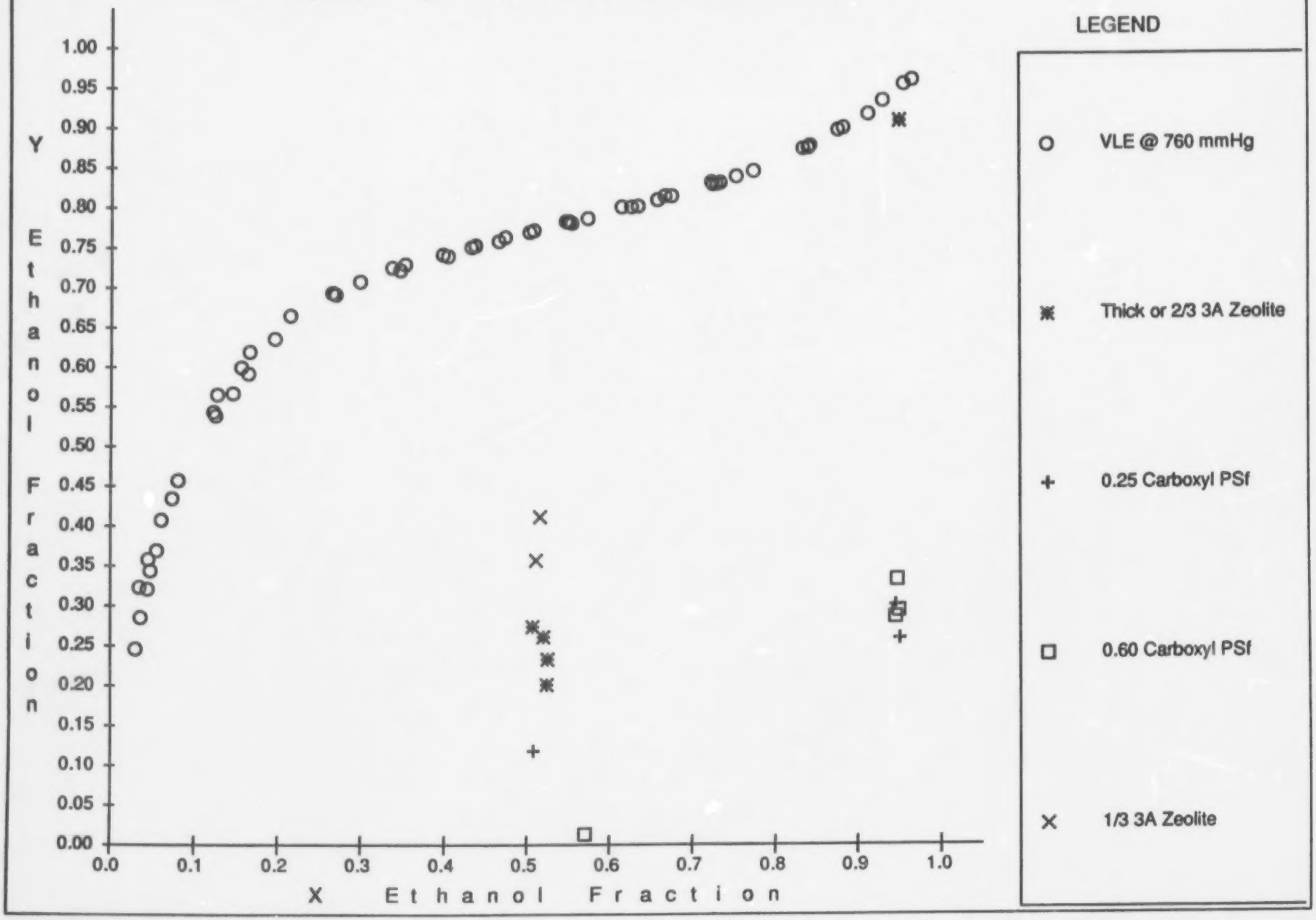
Separation results using 3A zeolite are summarized in Figure 28 in the form of an X(feed) versus Y(permeate or vapour) composition diagram, and are compared to separations achieved using carboxylated polysulfones, as well as vapour-liquid equilibrium at 760 mmHg. As can be seen in this diagram, the 3A zeolite was outperformed on the basis of water selectivity by Carboxylated Polysulfones at all concentration ranges investigated. And although the 3A zeolite did exhibit reasonably good water selectivity and flux at lower ethanol concentrations, it only exhibited slight selectivity at azeotropic feed concentrations where ability to dehydrate would be of most interest.

S-115 Zeolite - Organophilic:

While enhanced selectivity to water was found when using the hydrophilic 3A zeolite, no corresponding effect was found for the organophilic S-115. One film incorporating S-115 zeolite was run using feed near 50 percent ethanol: 2/3 S-115, 1/3 RTV 615, cyclohexane diluent, bottom skinned, coupon No.1. The nitrogen permeation, flux and separations results for this coupon are listed as follows:

Figure 28. Summary Comparison of Selectivity for Water Selective Films

Carboxylated Polysulfone and 3A Zeolite/Silicone



Coupon	Measured Thickness (μm)	Initial N2 Flux (mL/min)	Final N2 Flux (mL/min)	Estimated Thickness (μm)
2/3 S-115	145	3.00	2.90	20

Coupon	Run Sample	Temp (°C)	Flux (g/m^2h)	α_{ew} (-)
2/3 S-115	1	105	2560	0.80
	2	105	2480	0.73

The α_{ew} separation factor results are presented in Figure 29 compared with silicones alone, and in Figure 30 compared to relative volatility data from vapour-liquid equilibrium at 760 mmHg. It is apparent from these plots that the addition of the S-115 zeolite did not, as was anticipated, enhance selectivity to ethanol beyond that which was achieved by silicone alone. In fact, it produced a slight increase in selectivity to water. These results contrast sharply with those of Smolders where α_{ew} values for pervaporation were increased to as high as 40 by the addition of organophilic zeolites.

6.5.2 Ethanol Extractants

Following a similar tactic as employed with the zeolites, a number of liquid chemical species which exhibit selectivity for ethanol out of water in two-phase liquid extraction systems, were added to silicone with the intent of making in essence "liquid membrane" films which might exert specific selectivity for ethanol.

Films incorporating three extractants, which ranked in the top ten in a run of the Queen's University ethanol extractant database, were tested in the small cell system using feed mixtures near 50 percent ethanol. The films are described as follows:

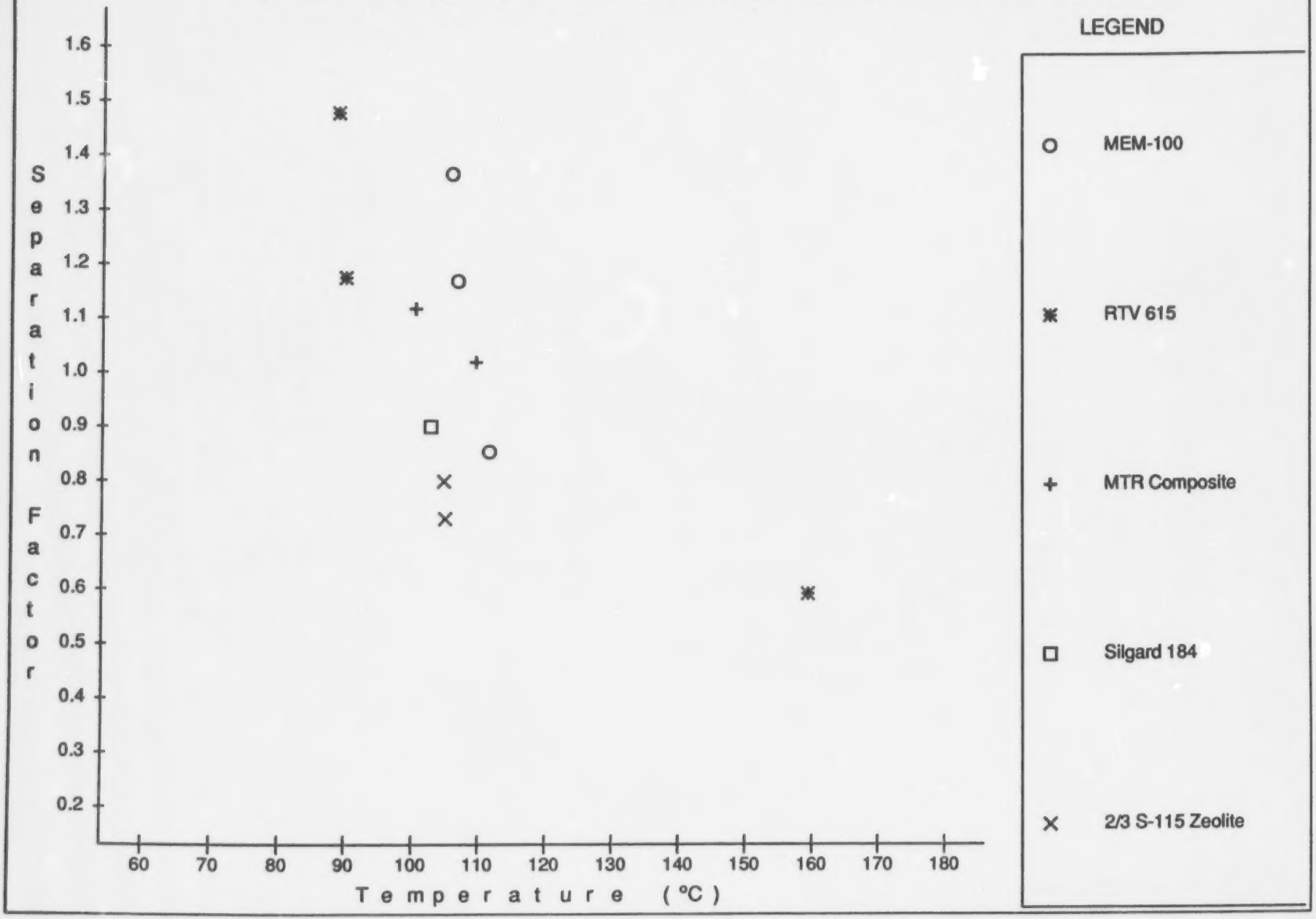
1. 1/3 diisopropyl-L-tartrate, 2/3 RTV 615, bottom skin, coupon No.3
2. 1/3 2-ethyl-1,3-hexanediol, 2/3 RTV 615, bottom skin, coupon No.4
3. 1/3 1,7-heptanediol, 2/3 RTV 615, bottom skin, coupon No.1

The initial and final nitrogen permeation fluxes, initial appearance, measured thicknesses, and thicknesses estimated from initial nitrogen permeation using the permeability coefficient for silicone, are listed as follows:

Coupon	Measured Thickness (μm)	Initial N2 Flux (mL/min)	Final N2 Flux (mL/min)	Estimated Thickness (μm)	Initial Appearance
D-L Tart	180	0.75	0.71	110	opaque
E-Hexdol	97	0.97	1.02	86	clear
Heptdiol	200	0.24	0.59	344(int)	white (int)
				141(fin)	clear (fin)

Figure 29. Selectivity of Silicone Films Incorporating S-115 Zeolite

Separation Factor [αew] as a Function of Temperature for Feed near 50% Ethanol



As in the case of the zeolite films, the thicknesses estimated from initial nitrogen permeation fluxes were less than measured thicknesses, except in the case of 1,7-heptanediol. The melting point of this material is 19°C. It can be presumed from the initial appearance of this film that it was in solid phase at that time, and appeared to exert some effect on nitrogen permeation. The appearance of this film when removed from the cell was clear, presumably as it was then in liquid phase, and its nitrogen permeation more paralleled that observed with the other films.

Flux and separation data obtained for these films using feed mixtures near 50 percent are listed as follows:

Coupon	Run Sample	Temp (°C)	Flux (g/m^2h)	α_{ew} (-)
D-L Tart	2	104	785	0.76
E-Hexdol	1	104	1290	0.86
	2	103	1010	0.89
Heptdiol	1	101	579	0.80
	2	101	589	0.82

A single run was also conducted in the larger cell system which employed an RTV 615 silicone film of 180 µm measured thickness incorporating 10 percent of the extractant 2-ethyl-1-hexanoic acid. Similar flux and separation results were obtained in this case, with a flux of 499 g/m^2h and α_{ew} of 0.82 at a temperature of 108°C.

The α_{ew} separation factor results for all the extractants are presented in Figure 31 compared with silicones alone, and in Figure 32 compared to relative volatility data from vapour-liquid equilibrium at 760 mmHg. As in the case of S-115 zeolite, these extractants did not have the desired effect of increasing selectivity to ethanol, instead produced a slight increase in selectivity to water. While permeates were not analyzed for extractants, their presence was not detected by odor, suggesting that even though the desired selectivity could not be attained, silicone films could be used as a means of immobilizing liquid species to form "liquid membranes".

6.5.3 Vacuum Operation at Lower Temperature

Three coupons were tested using 50 percent ethanol feed at a temperature of about 60°C. The feed was maintained in vapour phase by running with vacuum on the feed side as well as permeate side of the membrane. The three film coupons tested are listed as follows:

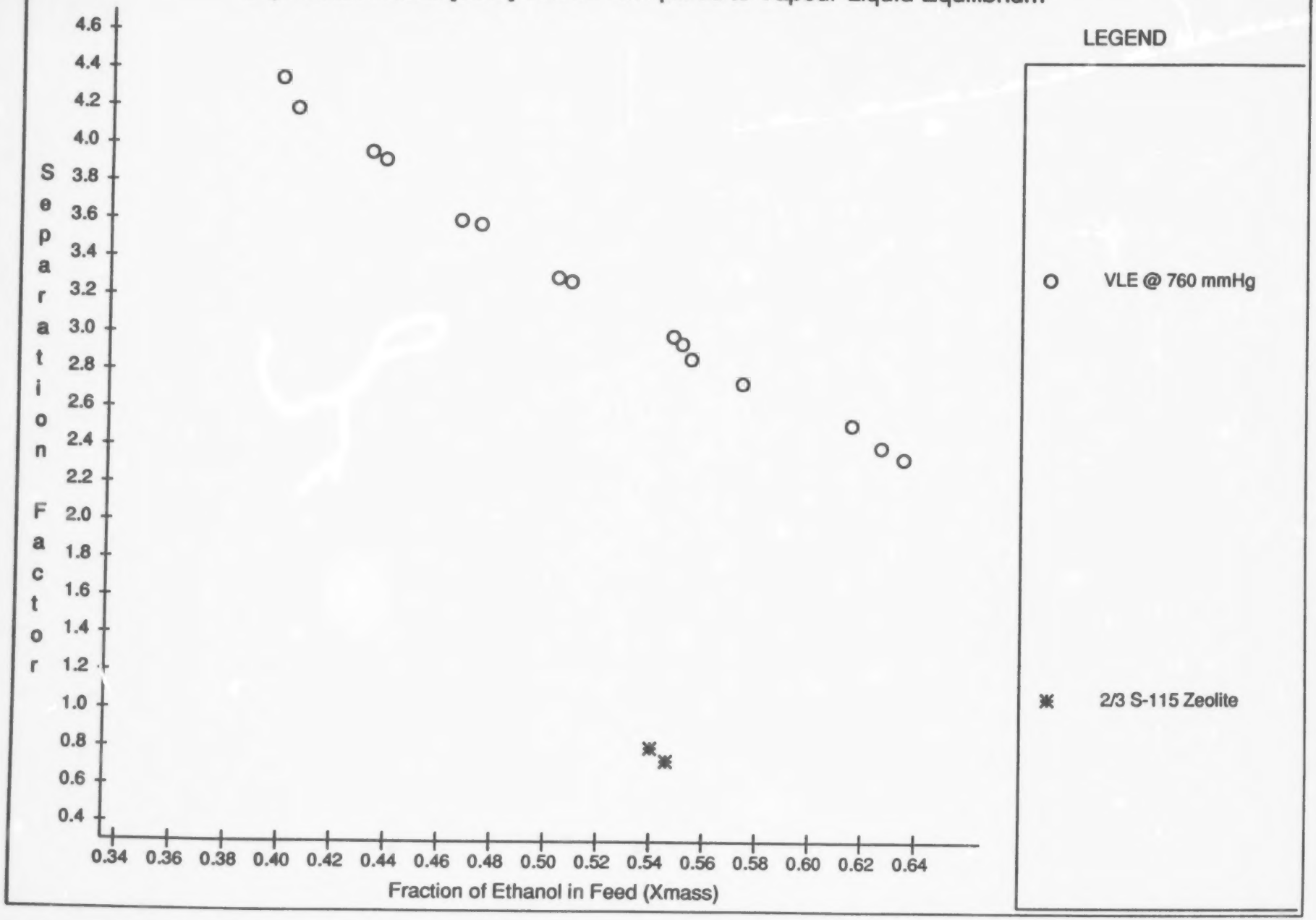
1. MEM-100 silicone of 3 mil (76 µm) thickness

2. 1/3 2-ethyl-1,3-hexanediol, 2/3 RTV 615, bottom skin, coupon No.1

3. 2/3 S-115, 1/3 RTV 615, cyclohexane diluent, bottom skinned, coupon No.2

Figure 30. Selectivity of Silicone Films Incorporating S-115 Zeolite

Separation Factor [αew] Values Compared to Vapour-Liquid Equilibrium



The nitrogen permeations observed for these films and their estimated effective thicknesses, based on initial fluxes, are listed as follows:

Coupon	Measured Thickness (μm)	Initial N2 Flux (mL/min)	Estimated Thickness (μm)
MEM-100	76	0.67	124
E-Hexdol	94	0.56	146
2/3 S-115	150	3.00	20

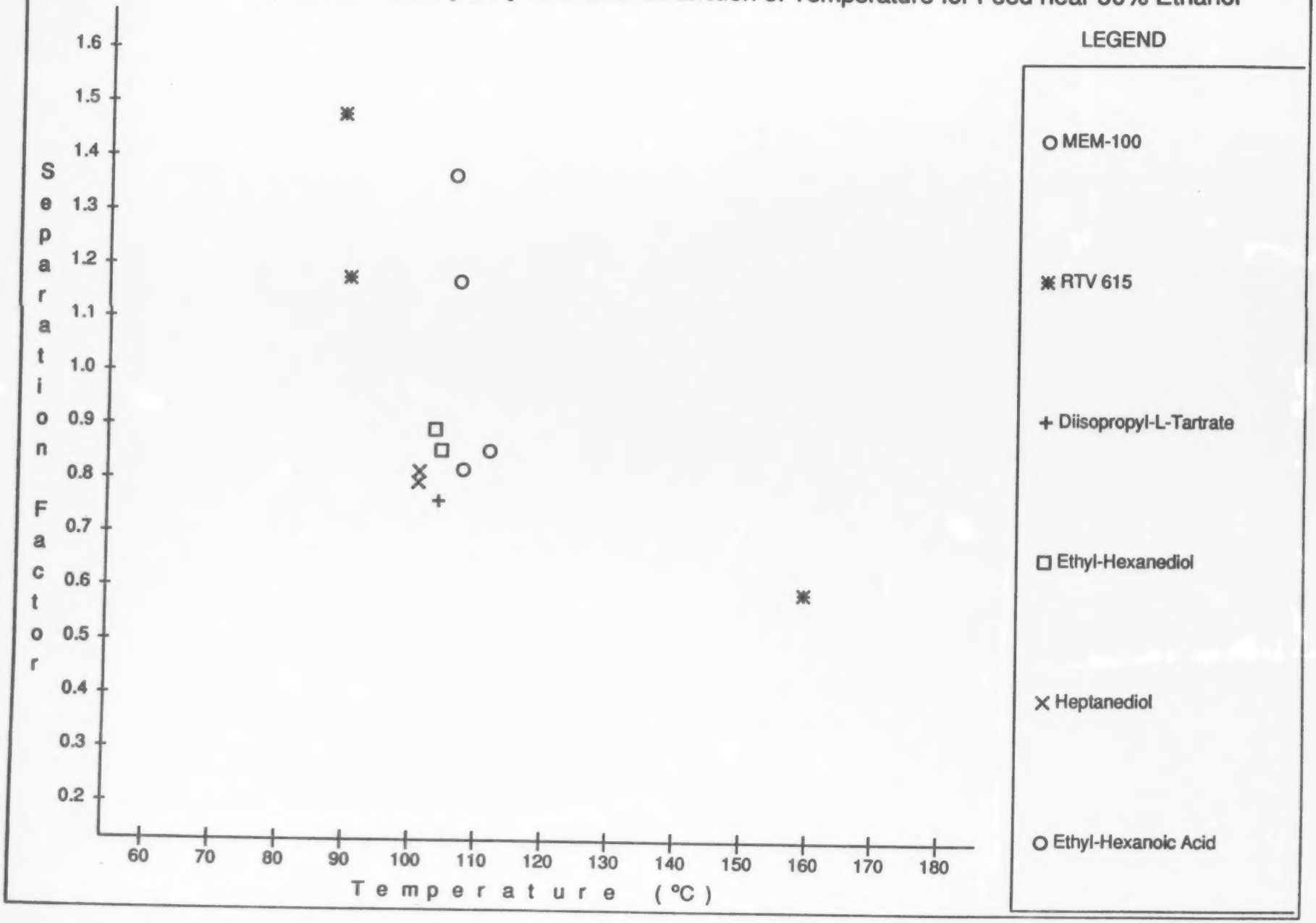
The first coupon to be run was the silicone film without additive. Enhancement of ethanol was achieved in the permeate to a level of about 80 percent. It was observed, however, that there was a significant vapour-liquid equilibrium effect within the cell since a significant volume of liquid was found to have been retained in the cell which had a much lower ethanol content than the feed. Noting this, films incorporating S-115 silicalite and ethyl hexanediol were also run under virtually identical results. Flux and separation results for the three films are listed as follows:

Coupon	Run Sample	Temp (°C)	Flux (g/m^2h)	α_{ew} (-)	Pressure (mmHg)
MEM-100	1	60	533	3.33	296
E-Hexdol	1	62	243	2.54	299
2/3 S-115	1	64	1190	3.19	351

The separation results are compared in Figure 33 with relative volatility values from vapour-liquid equilibrium at 380 and 190 mmHg total pressure. As can be seen in this diagram, the addition of either organophilic zeolite or extractant achieved selectivity to ethanol that was neither better than silicone alone nor better than that which could be achieved under similar pressure conditions by vapour-liquid equilibrium.

Figure 31. Selectivity of Silicone Films Incorporating Ethanol Extractants

Separation Factor [α_{ew}] Values as a Function of Temperature for Feed near 50% Ethanol



7.0 DISCUSSION

7.1 Ethanol Selective Membranes

The primary objective of the study was to attempt to develop a potential commercial process for the energy-efficient concentration of ethanol using membranes selectively permeable to ethanol in the vapour phase. This objective could not be fulfilled because selectivity to ethanol in the vapour phase could not be achieved.

A number of hydrophobic polymers were tested which nevertheless appeared to exert selectivity to water. Parylene C, with one of the lowest water vapour permeability coefficients reported, and Neoprene were of particular note in this regard. The best selectivity achieved was by Silicone rubber, and even this was well below what could be achieved simply through vapour-liquid equilibrium. The case with Silicone rubber also demonstrated strong dependence of the α_{ew} separation factor on concentration and temperature, both of which appeared to work against selective concentration of ethanol. At feed concentrations near 50 percent, the selectivity was shown to decline as a function of temperature. At 95 percent (azeotropic) feed concentrations, virtually no selectivity could be achieved at all (i.e. $\alpha_{ew} = 1.0$). This result suggested that even though a silicone membrane could be used to concentrate ethanol at lower concentrations, although not very well, it would still not be able to concentrate beyond the azeotrope.

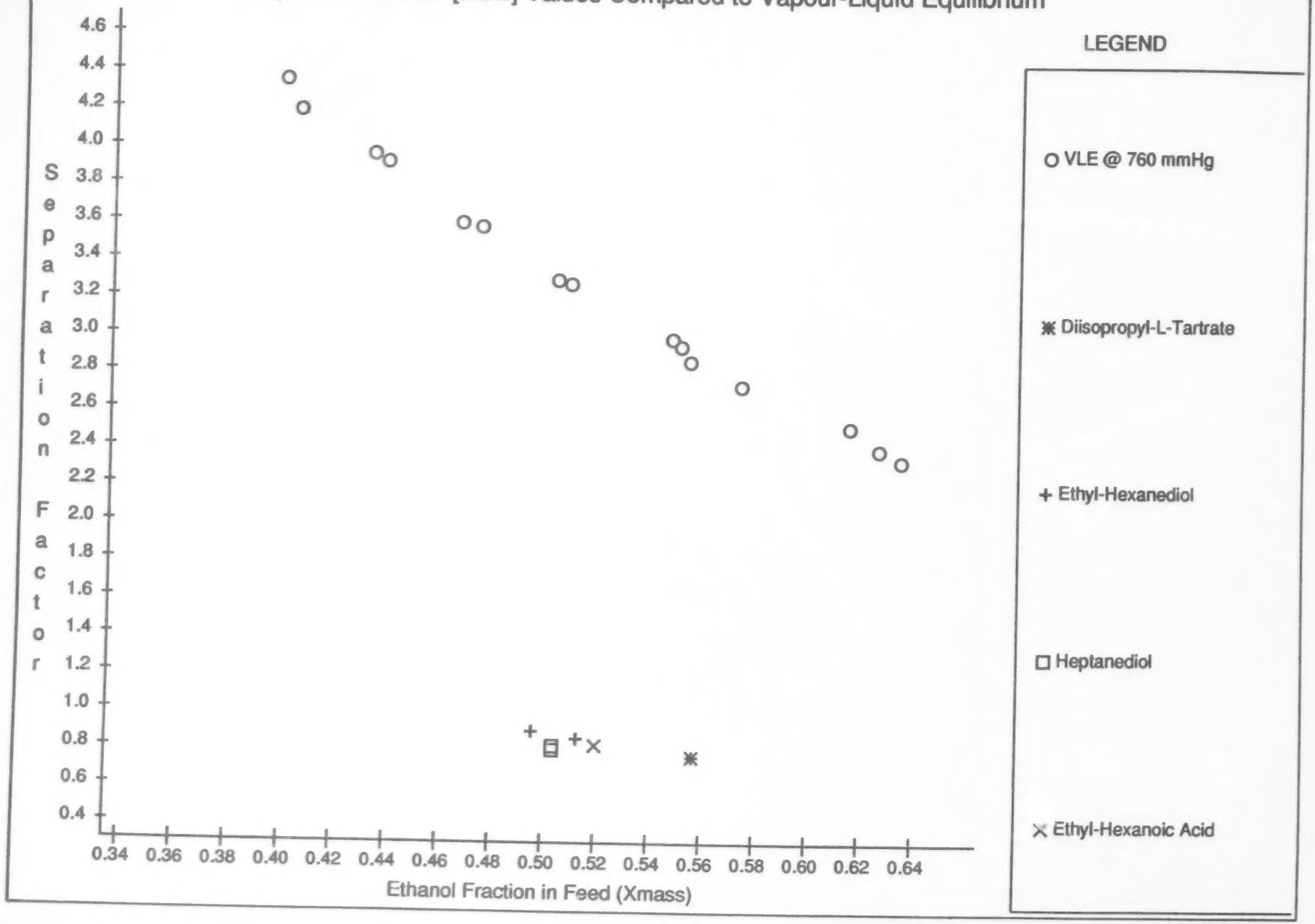
Attempts were made to enhance selectivity by the addition of ethanol selective agents to silicone, however, this work did not produce the desired selectivity. Addition of organophilic zeolites was reported in the literature to dramatically increase ethanol selectivity in pervaporative processes by increasing selective adsorption of the ethanol species. In this study, no enhancement of ethanol selectivity was achieved in vapour phase membrane separation by the addition of either organophilic zeolite or ethanol selective, high boiling point extractants. The result, if anything, was a slight increase in water selectivity. The addition of water selective zeolites on the other hand did produce pronounced selectivity to water at lower ethanol concentrations near 50 percent. In this case as well, water selectivity appeared to be concentration dependent with only very slight selectivity achieved when using azeotropic feed.

An attempt was also made to run silicone and silicone/additive films under vacuum at lowered temperatures. Although higher selectivities were found, they were the result of vapour-liquid equilibrium effects, and no enhancement beyond equilibrium was achieved. Again, the result of adding ethanol selective agents was if anything a slight increase in water selectivity.

Although no positive results were achieved for the selective separation of ethanol from water in vapour phase, the results of the study may still cast some light on the mechanisms of transport and selection involved in vapour phase transport, which are still not well

Figure 32. Selectivity of Silicone Films Incorporating Ethanol Extractants

Separation Factor [αew] Values Compared to Vapour-Liquid Equilibrium



understood.

The apparent lack of selectivity toward ethanol was the major problem, but was not the only problem encountered. A secondary, but still important problem, was that of materials incompatability of the polymers to the high temperature vapour environment, especially when vapour ethanol was involved. Degradation of polymer films was apparent in all but a few cases.

Materials incompatability was particularly problematic with the Udel and modified Udel polysulfones. Udel polysulfone itself was found to be destroyed by vapour ethanol in a catastrophic manner. The hydrophobic di(trimethylsilyl) modified version was similarly affected. The hydrophobic di(butyl) and hydrophilic di(hydroxy) versions were also badly affected, but to a much less dramatic extent. Victrex polysulfone appeared to survive exposure, but with some adverse effects as evidenced by the increase in nitrogen permeation. One modified version of Udel did, however, exhibit much improved solvent resistance. This was the hydrophilic carboxylated polysulfone.

7.2 Water Selective Carboxylated Udel Polysulfone

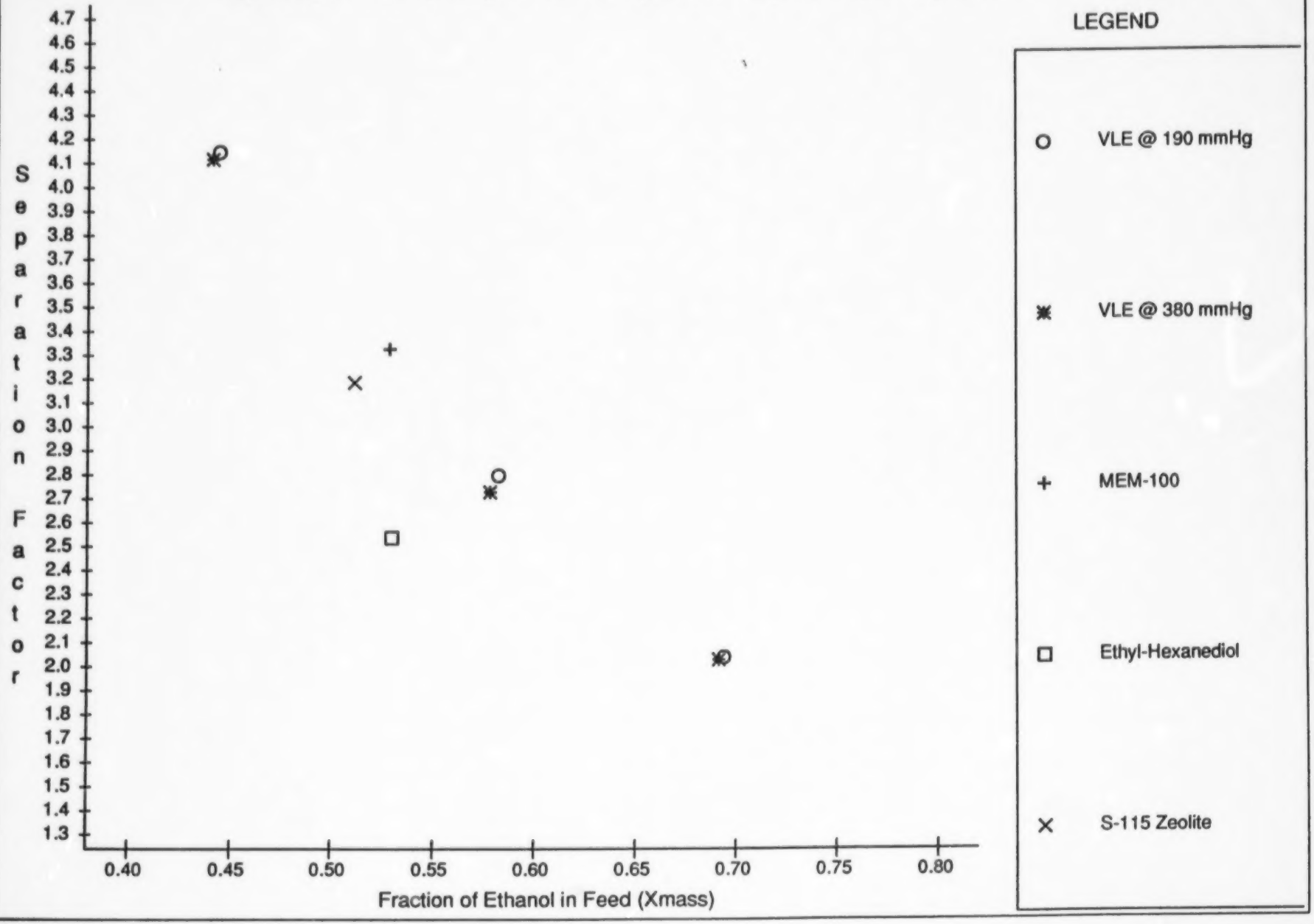
While the major purpose of the project could not be achieved, some very successful results were obtained. The carboxylated Udel polysulfones, aside from exhibiting good resistance to the solvent ethanol environment, appeared to exert fairly strong selectivity, albeit toward water, with vapour phase feed mixtures. Although the few runs conducted with this material were still preliminary in nature, they confirmed that this polymer was selective to water, and also indicated that the selectivity might be related to the degree of carboxyl group substitution. This latter finding suggested that the selectivity to water could potentially be improved by increasing the number of carboxyl groups substituted per polymer repeat unit. The results with the carboxylated Udel represented a major positive finding, with potential for commercial development in a vapour phase dehydration system.

A dehydration operation requires the selective removal of a small portion of the feed (i.e. the five percent water in an azeotropic mixture) along with as little product as possible. Thus given the usual trade-off which occurs to some extent in gas systems, between selectivity and flux, the maintenance of high selectivity is more important than attaining high flux. The Carboxylated Polysulfone exerted a strong selectivity with some potential apparent for improvement.

A preliminary estimate was made, as presented in Table 2, to determine the minimum membrane flux necessary to compete with the capital cost of a zeolite packed bed dehydration system, which is known to be less costly than azeotropic distillation systems. This estimate was based on achieving an α_{we} of 44 for azeotropic feed, which was actually achieved in experimentation (i.e. permeate concentration of 30 percent ethanol from 95 percent ethanol feed.) The resulting minimum estimated

Figure 33. Operation of Silicone Films with Selective Agents under Vacuum

Separation Factor [αew] Values Compared to Vapour-Liquid Equilibrium



flux of 160 g/m^2h was virtually achieved in experiments at the laboratory scale.

It could thus be inferred that a membrane dehydration system incorporating carboxylated polysulfone could be cost competitive with zeolite dehydration systems. Further, this new system would have other advantages. It would operate in a continuous, as opposed to cyclic manner. If membranes could be made to last for several years before needing replacement, it could offer lowered maintenance and operator requirements. It could also be more energy efficient since energy would not have to be expended for regeneration as in the case of zeolites.

In terms of energy consumption, such a membrane system would be definitely more efficient than azeotropic distillation and probably more efficient than pervaporation. As in the case of pervaporation, a major energy, and capital cost input would be the vacuum pump system. Unlike pervaporation, however, heating requirements would only be associated with maintaining the vapour in that phase, as opposed to the phase change involved with pervaporation (i.e. sensible versus latent heat requirements for water removed), and could be anticipated to be much smaller.

Given the preliminary nature of the experimental results, no further detailed economic or energy estimates were conducted for the dehydration system.

Carboxylated polysulfone represents a completely novel polymer that may compete favourably with other developing technologies in vapour phase dehydration. However, four important questions remain unresolved from the experiments conducted. These can be listed as follows:

1. Will increasing the degree of carboxylation of the polymer increase the selectivity of the membrane to water?

   This relationship was found at lower ethanol concentrations, but was indeterminant at azeotropic feed concentrations where it is most important.

2. Will the membrane provide effective dewatering?

   Experiments employed large flows past the membrane such that there was little if any percieved change in the concentration of ethanol from the feed to the retentate (non-permeate). This question also addresses concentration dependence, whether the membrane would continue to be as selective to water as the concentration of ethanol approached 100 percent, and temperature dependence of selectivity.

3. To what extent will selectivity of the membrane be retained in moving to somewhat thinner skinned asymmetric membranes with higher flux?

   This question addresses the trade off usually encountered between

TABLE 2

PRELIMINARY ECONOMIC ESTIMATE OF
MINIMUM MEMBRANE FLUX TO COMPETE WITH ZEOLITE DEHYDRATION

Basis of Comparison

Plant of 10,000,000 L/y or approximately 980 kg/h anhydrous ethanol.

Zeolite Dehydration System Cost

From Garg and Yon (1986) estimated Capital Cost
0.055 - 0.075 USD86/USGal/year Capacity
Capital Cost is estimated as 200,000 CAD88
Operating Cost is estimated as 65,000 CAD88/year
(of which Adsorbant represents 45,000 CAD88/year)

Membrane System Cost per Unit Area

In Peinemann et. al. (1986), the cost of a system to recover approximately 1,000 L/d of solvents from hot air was discussed with an estimated total system cost of 331 USD84/m^2.

This system would be fairly similar to that required to dehydrate ethanol vapour, and reflects the major added capital cost for such a system, being the vacuum pump. Using this value as a capital cost basis the unit membrane area cost was estimated to be 440 CAD88/m^2.

Estimated Maximum Membrane Area

Using the estimated capital of 200,000 CAD88 for a zeolite dehydration system as maximum capital available, the maximum membrane area is estimated as follows:

$$200{,}000 \text{ CAD}/440 \text{ CAD}/m^2 = 460 \ m^2$$

Estimated Minimum Permeate Flow Rate

Assuming flow to dehydration unit is 95 percent ethanol; α_{ew} is 44 and unaffected by concentration such that permeate is 30 percent ethanol; and all water is removed as permeate, the minimum permeate flow is estimated as follows:

$$80 \text{ kg/h} * 0.05/0.95 * 1/0.70 = 74 \text{ kg/h of Permeate}$$

Estimated Minimum Permeate Flux

From minimum necessary permeate flow and maximum available area, an estimated minimum flux is estimated as follows:

$$74 \text{ kg/h}/460 \ m^2 = 0.16 \text{ kg}/m^2h \text{ or } 160 \text{ g}/m^2h$$

flux and selectivity in gas systems, although as mentioned earlier, only somewhat higher fluxes may be required. An interesting point in this regard may be the use of silicone for surface coatings. This procedure is now a fairly conventional technique in gas separation. As was demonstrated in the study, silicone is virtually unselective at high ethanol concentrations, and can be induced at lower ethanol concentrations to be slightly selective to water, by increasing the operating temperature.

4. Would the membrane have adequate strength, and chemical resistance to allow construction of a module of practical size?

   While the carboxylated polysulfone had better resistance to ethanol vapour, breakage was still noted in some cases (not during but after exposure). The nature of the cause of breakage would have to be determined in order to obviate this problem.

Carboxylated Udel polysulfone showed promise as a potential membrane material suitable for a vapour phase dehydration system. As was noted, considerable work needs to be completed at the laboratory stage to verify and optimize its performance. This work would be most efficiently conducted at the laboratories of the Chemical Engineering Section of the National Research Council of Canada in order to best take advantage of their membrane materials production expertise, their expertise in membrane manufacture, and the test cell systems and other relevant equipment already in place.

8.0 CONCLUSIONS

1. Vapour phase selectivity to ethanol could not be adequately attained.

2. Strong water selectivity and enhanced solvent resistance were found with hydrophilic carboxylated Udel polysulfone.

3. Further experimentation is warranted toward development of a cost-effective vapour phase dehydration system based on carboxylated Udel polysulfone membranes.

9.0 RECOMMENDATIONS

1. It is recommended that this project continue to a next phase focusing on development of a vapour-phase dehydration system employing water selective carboxylated Udel polysulfone membranes.

2. It is recommended that work in the next phase continue to be conducted at a laboratory scale in order to resolve the outstanding technical questions regarding membrane performance.

3. It is recommended that the next phase also be carried out at laboratories of the Chemical Engineering Section of the Division of Chemistry, National Research Council of Canada.

LIST OF REFERENCES

Asaeda, M. and L.D. Du. 1986. Separation of Alcohol/Water Gaseous Mixtures by Thin Ceramic Membrane. Journal of Chemical Engineering of Japan. 19 (1): 72-85.

Barrie, J.A. 1986. The Transport of Water in Polymers. in Membranes in Gas Separation and Enrichment Proceedings of the Fourth BOC Priestley Conference. Royal Society of Chemistry.

Baker, R.W. and I. Blume. 1986. Permselective Membranes Separate Gases. Chemtech. 16 (April): 232-238.

Baker, R.W. and I. Blume. 1987. Separation and Concentration of Organic Solvents from Water Using Pervaporation.

Baker, R.W., N. Yoshioka, J.M. Mohr and A.J. Khan. 1987. Separation of Organic Vapors from Air. Journal of Membrane Science. 31: 259-271.

Baker, R.W., I. Blume, V. Helm, A. Khan, J. Maguire and N. Yoshioka. 1984. Membrane Research in Energy and Solvent Recovery from Industrial Effluent Streams. Membrane Technology and Research Inc. U.S. Department of Energy Report DE4016819.

Bakisk, R. and W. Schneider. 1986. Modelling of Transport Phenomena in Pervaporation Membranes. in: Proceedings of the First International Conference on Pervaporation Processes in the Chemical Industry. ed. R. Bakish. Bakish Materials Corporation. Englewood.

Barrie, J.A. 1986. The Transport of Water in Polymers. in: Proceedings of the Fourth BOC Priestley Conference. pp 89-113.

Breck, D.W. . Zeolite Molecular Sieves. Wiley. New York.

Campbell, I.M. 1983. Biomass, Catalysts and Liquid Fuels. Technomic. Lancaster.

Changluo, Z., L. Moe and X. Wei. 1987. Separation of Ethanol-Water Mixtures by Pervaporation-Membrane Separation Process. Desalination. 62: 299-313.

Eustache, H. and G. Histi. 1981. Separation of Aqueous Organic Mixtures by Pervaporation and Analysis by Mass Spectrometry or a Coupled Gas Chromatograph-Mass Spectrometer. Journal of Membrane Science. 8: 105-114.

Flanigen, E.M., J.M. Bennet, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner and J.V. Smith. 1978. Silicalite, a new Hydrophobic Crystalline Silica Molecular Sieve. Nature. 271 (5645): 512-516.

Garg, D.R., and C.M. Yon. 1986. Adsorptive Heat Recovery Drying System. Chemical Engineering Progress. February. 54-60.

Goncalves, M.D.C., G.D.S.S. Marques and F. Galembeck. 1983. Pervaporation and Dialysis of Water-Ethanol Solutions using Silicone Rubber Membranes. Separation Science and Technology. 18 (10): 893-904.

Tuiver, M.D., O. Kutowey, W.A. McCurdy and J.W. ApSimon. 1986. Novel Polysulfones for Membrane Applications. Proceedings of the International Membrane Conference on the 25th Anniversary of Membrane Research in Canada. Ottawa, September 1986. ed. Malaiyandi, Kutowey and Talbot. pp 187-202.

Guiver, M.D., J.W. ApSimon, and O. Kutowey. 1988. The Modification of Polysulfone by Metalation. Journal of Polymer Science, Polym. Lett. Ed. 26: 123-127.

te Hennepe, H.J.C., D. Bargeman, M.H.V. Mulder and C.A. Smolders. 1987. Pervaporation with Zeolite filled Silicone Rubber Membranes in: Proceedings of the Second International Conference on Pervaporation Processes in the Chemical Industry, pp. 71-78.

Heisler et. al. 1956. Science. 124: 77.

Hoffman, E., D.M. Pfenning, E. Philippsen, P. Schwahn, M. Sieber, R. Wehn, D. Woermann and G. Wiedner. 1987. Evaporation of Alcohol/Water Mixtures through Hydrophobic Porous Membranes. Journal of Membrane Science. 34: 199-206.

Hoover, K.C. and S.T. Hwang. 1982. Pervaporation by a Continuous Membrane Column. Journal of Membrane Science. 10: 253-271.

Kimura, S. and T. Nomura. 1982. Pervaporation of Alcohol-Water Mixtures with Silicone Rubber Membrane. Membrane. 7 (6): 353-354.

Kirk-Othmer Encyclopedia of Chemical Technology, 1981. 3rd Edition. Wiley and Sons, New York, Volume 15.

Klien, S.M. and W.H. Abraham. 1983. Adsorbtion of Ethanol and Water Vapors by Silicalite. in: Adsorbtion and Ion Exchange - '83. AIChE Symposium Series. Vol. 79, No. 230. pp 53-59.

Kollerup, F. and A.J. Daugulis. 1985. Screening and Identification of Extractive Fermentation Solvents using a Database. Canadian Journal of Chemical Engineering. 63: 919-597.

Leeper, S.A. 1986. Membrane Separations in the Production of Alcohol Fuels by Fermentation. in Membrane Separations in Biotechnology. ed. W.C. McGregor. Marcel Dekker. New York.

Leeper, S.A. and G.T. Tsao. 1987. Membrane Separations in Ethanol Recovery: An Analysis of Two Applications of Hyperfiltration. Journal of Membrane Science. 30: 289-312.

Lonsdale, H.K. 1987. The Evolution of Ultrathin Synthetic Membranes. Journal of Membrane Science. 33: 121-136.

Masuda, T., B.Z. Tang and T. Higashimura. 1986. Ethanol-Water Separation by Pervaporation through Substituted-Polyacetylene Membranes. Polymer Journal. 18 (7): 565-567.

Matson, S.L., J. Lopez and J.A. Quinn. 1983. Separation of Gases with

Synthetic Membranes. Chemical Engineering Science. 38 (4): 503-524.

Mazid, M.A. 1984. Mechanisms of Transport through Reverse Osmosis Membranes. Separation Science and Technology. 19 (6&7): 357-373.

McNair, H.M., and E.J. Bonelli. 1968. Basic Gas Chromatography. Varian. Berkeley.

Mulder, M.H.V., J.O. Hendrikman, H.Hegeman and C.A. Smolders. 1983. Ethanol-Water Separation by Pervaporation. Journal of Membrane Science. 16: 269-284.

Nakamura, A. and H. Makino. 1987. Applications of the Aromatic Polyimide Membranes: I Dehydration by Vapour Phase Permeation Process. Membrane. 12 (5): 289-292.

Nakao, S.I., F. Saitoh, T. Asakura, K. Toda and S. Kimura. 1987. Continuous Ethanol Extraction by Pervaporation from a Membrane Bioreactor. Journal of Membrane Science. 30: 273-287.

Neel, J. 1986. Fundamentals and General Chemical Engineering Aspects of Pervaporation. In: Proceedings of the First International Conference on Pervaporation in the Chemical Industry. ed. R. Bakish. pp 10-40.

Peinemann, K.V., J.M. Mohr, and R.W. Baker. 1986. The Separation of Organic Vapors from Air. In: Recent Advances in Separation. AIChE Symposium Series Vol. 82, No. 250. pp 19-26.

Rautenbach, R. and R. Albrecht. 1987. Pervaporation and Gas Permeation - Fundamentals of Process Design. International Chemical Engineering. 27 (1): 10-24.

Rautenbach, R. and U. Meyer-Blumenroth. 1987. Vapour Permeation of Water/Organic Mixtures. Internatinal Membrane Conference. Tokyo, Japan.

Rogers, C.E. 1985. Permeation of Gases and Vapours in Polymers. In: Polymer Permeability. ed. J. Comyn. Elsevier. New York.

Rogers, C.E., M. Fels and N.N. Li. 1972. Separation by Permeation through Polymeric Membranes. In: Recent Developments in Separation Science. Volume II. Chemical Rubber Company. Cleveland.

Sanyo Chemical Industries. Japanese Patent 60,78,601. May 5, 1985.

Schissel, P. and R.A. Orth. 1984. Separation of Ethanol-Water Mixtures by Pervaporation through Thin, Composite Membranes. Journal of Membrane Science. 17: 109-120.

Sheng, J., J.C. Mora, M. Emami, R.S. Bes and P. Aptel. 1986. Pervaporation in Hollow Fiber Bundles: Heat and Mass Transfer in a Unit. Proceedings of World Congress III of Chemical Engineering. Tokyo.

Sodeck, G. and F. Hannak. 1986. Experience with Pervaporation Plants. In: Proceedings of the First International Conference on Pervaporation Processes

in the Chemical Industry. ed. R. Bakish. Bakish Materials Corporation. Englewood.

Spangler, G.E. 1975. Analysis of two membrane inlet systems on two potential trace vapour detectors. American Laboratory. 7 (July): 36-45.

Suematsu, H., K. Harada and T. Kataoka. 1987. Separation of Ethanol-Water Mixtures using Silicone Rubber Membrane. Membrane. 12 (2): 95-100.

Uragami, T. and M. Saito. 1987. Permeation and Separation Characteristics of Alcohol Aqueous Solutions through Hydrophilic Polymer Membranes. Internatinal Membrane Conference. Tokyo, Japan.